

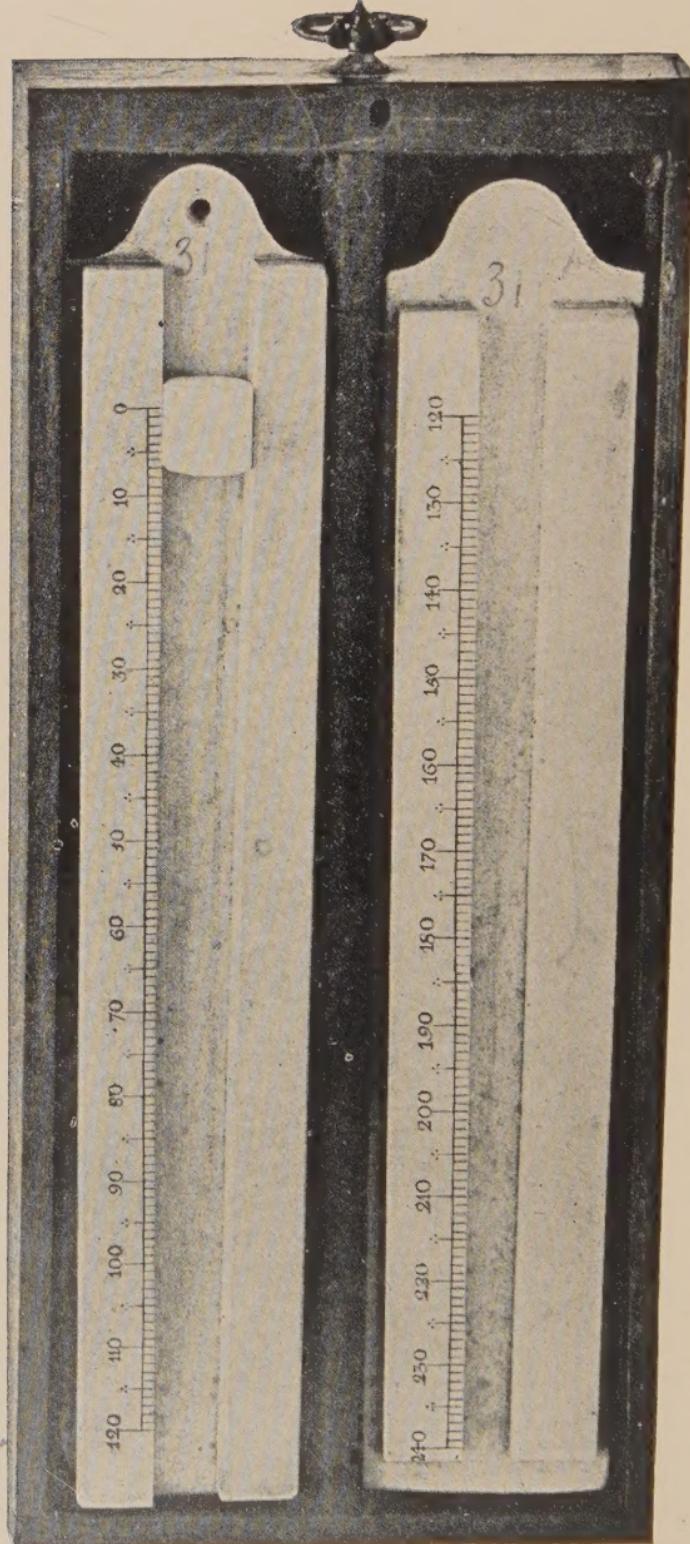
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Thermodynamics and Chemistry.

A Non-Mathematical Treatise for Chemists and Students of Chemistry. By P. DUHEM, Correspondant de l'Institut de France, Professor of Theoretical Physics at the University of Bordeaux. Authorized Translation by GEORGE K. BURGESS, Docteur de l'Université de Paris, Assistant Physicist, Bureau of Standards. 8vo, xxi + 445 pages, 139 figures. Cloth, \$4.00.

High-Temperature Measurements.

By H. LE CHATELIER, Ingénieur en chef du Corps des Mines, Professor de chimie minérale au Collège de France, and O. BOUDOUARD, Assistant, Collège de France. Translated by GEORGE K. BURGESS, D.Sc. (Paris), Assistant Physicist, Bureau of Standards. Second Edition, Revised and Enlarged. 12mo, xv + 341 pages, 79 figures. Cloth, \$3.00.



Frontispiece.

HIGH-TEMPERATURE MEASUREMENTS.

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AUTHOR'S PREFACE TO FIRST AMERICAN EDITION.

THE measurement of high temperatures was considered for a long time to be a very difficult operation and of a very uncertain precision. There were cited with admiration a half-dozen determinations seeming to merit some confidence. During the last few years the question has made considerable progress, and we possess to-day several sufficiently precise pyrometers whose usage is rapidly spreading among scientific and industrial laboratories. Before describing them, perhaps it will not be useless to indicate the services that they may render to science and to industry, by giving a brief summary of similar services that they have already rendered.

Among the researches in pure science which result from the new methods of the measurement of high temperatures, of primary importance are the masterly investigations of Osmond on the allotropic transformations of iron. After having precisely determined the nature of the phenomenon of recalcitrance, noted for the first time by Gore and Bartlett, Osmond discovered in iron two similar transformations: one, taking place in the neighborhood of 750° , corresponds to the loss of magnetic properties, and the other, at about 900° , is accompanied by a considerable evolution of heat. A third transformation of iron near

1300° has been discovered since by Ball. Soon after, Curie studied by the same methods the variation with the temperature of the magnetic properties of a great number of substances, iron among them, which possess very definite perturbations corresponding to the different transformation-points.

Later, Le Chatelier studied the influence of temperature on the dilatation and electrical resistance of metals. The allotropic transformations are recognized by sharp points in the curves of electrical resistance and by sudden depressions in the dilatation curves.

But these researches have not been limited to the metals and their alloys. Investigating the dilatation of the different varieties of silica, Le Chatelier was led to the discovery of a transformation of quartz at 580°, above which the dilatation of this substance becomes negative, and to the discovery, still more important, of a new variety of silica distinct from tridymite, but possessing the same density and into which silex and even quartz are transformed by sufficient heating.

In the same manner have been studied the dissociation of the carbonate of lime, the bromide of barium, of minium, etc. Similarly the curves of fusibility of salt mixtures have been determined, their forms indicating the existence of definite compounds or of solid solutions. Also it has been possible to distinguish, among the natural products classed under the general head clay, a series of distinct chemical substances.

Finally, it has been possible to pursue the study of the laws of radiation at high temperatures with a greater precision, and to establish the theory of incandescent enclosures.

If we take up next the researches in industrial science, we find the number to be so considerable that it is out of

the question to attempt to give in this short preface the complete list. It will suffice to mention the most important among them, such as the following investigations:

The fusibility of metallic alloys has been the object of a very complete memoir by H. Gautier, and of important researches by the late Sir Roberts Austen and by Heycock and Neville, Boudouard and others.

The tempering of steel has been examined in all its details by Osmond, Charpy, H. Howe, Sauveur, Brinnel.

Cementation by Arnold.

Crystallization in the annealing of metals, in particular of iron and brass, observed by Sauveur, Stead, Charpy.

And lastly the considerable number of researches made at the laboratory of the Ecole des Mines on the dilatation of ceramic pastes and of glass, by Damour, Chatenet, Grenet, Coupeau, Chautepié.

Precise methods for the measurement of high temperatures are not limited to laboratory researches, however, but have rapidly penetrated into industrial practice. A series of investigations by Le Chatelier first made known the exact temperatures entering into the various metallurgical operations; and to-day, in the greater number of steel-works, the tempering and the annealing of the great forged pieces, cannons, plates, are no longer made without the aid of pyrometers, doing away with the workman's judgment, formerly alone consulted.

In glass manufacture Damour has introduced the employment of pyrometers for controlling the large furnaces and recipients, and for the regulating of the temperature of the annealing-chambers.

Parvillé has done the same for the porcelain industry, where the use of fusible cones allowed the determination of the stopping-point of the heating but gave no continuous indications necessary to regulate the time of heating,

and on this last depends in a large measure the quality of the products obtained, and above all the cost of fuel.

In the manufacture of chemical products the precise measurements of temperature render to-day very great services; for instance, in the Deacon process for the making of chlorine, whose yield varies very greatly for slight changes of temperature. Ludwig Mond in England and the St. Gobian Company in France have the merit of having first utilized these new scientific methods.

Euchène of the Paris Gas Company controlled all the details of the manufacture of gas by numerous measurements of temperature.

But the most remarkable of these industrial applications have been made in England under the lead of Sir Roberts Austen by applying photographic recording to the indications of the thermoelectric pyrometer. Such installations at the Clarence Works of Sir Lothian Bell and at the blast-furnaces of Dowlais give a continuous record of the temperature of the draft and of the escaping gases.

These very considerable results have been obtained within less than ten years, although the new methods of temperature measurement were known as yet to only a few scientists and engineers. It is plausible to suppose that their influence on the progress of science and industry will be still greater during the coming years.

In finishing this preface, allow me to thank Dr. G. K. Burgess for having taken the trouble to translate into English our little volume. His science and his competence are for us a certain guarantee of cordial reception by American and English readers.

H. LE CHATELIER.

PARIS, January 10, 1901.

PREFACE TO SECOND EDITION.

THE subject of pyrometry has advanced very rapidly in recent years, and in preparing a new edition of the HIGH TEMPERATURE MEASUREMENTS, it has been necessary to completely revise the work. This revision has been made by the translator at the request of Prof. Le Chatelier, and the plan followed has been to leave the original text intact as far as possible and to insert the results of recent work in the appropriate chapters, all of which have been so modified.

The greatest advances have been made in optical pyrometry, and the chapter on this subject has been greatly extended and preceded by one on the laws of radiation. This material is largely taken from a paper * by Drs. Waidner and Burgess, and the latter desires to express his indebtedness to Dr. Waidner for permission to use this material.

Considerable additions have been made to the chapters on Electrical Resistance, Thermoelectric and Gas Pyrometry. Brief descriptions have been added of some other pyrometers which have been considerably used in the industries, especially in the United States. The impor-

* C. W. Waidner and G. K. Burgess: *Optical Pyrometry*, Bulletin of the Bureau of Standards, 1, No. 2, 1904.

tance of standardizing pyrometers has been emphasized by a special chapter devoted to that subject.

The translator wishes to express his thanks to those who have aided him by suggestions or data, and especially to Dr. Heraeus, Prof. H. M. Howe, Dr. Waidner, and Mr. Whipple of the Cambridge Company.

GEO. K. BURGESS.

WASHINGTON, September 6, 1904.

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HIGH TEMPERATURES.

INTRODUCTION.

WEDGWOOD, the celebrated potter of Staffordshire, the inventor of fine earthenware and of fine china, was the first to occupy himself with the exact estimation of high temperatures. In an article published in 1782, in order to emphasize the importance of this question, he considered at length certain matters a study of which would be well worth while even to-day.

“The greater part of the products obtained by the action of fire have their beauty and their value considerably depreciated by the excess or lack of very small quantities of heat; often the artist can reap no benefit from his own experiments on account of the impossibility to duplicate the degree of heat which he has obtained before his eyes. Still less can he profit from the experiments of others, because it is even less easy to communicate the imperfect idea which each person makes for himself of these degrees of temperature.”

Joining example to precept, Wedgwood made for his personal use a pyrometer utilizing the contraction of clay. This instrument, for nearly a century, was the only guide in researches at high temperatures. Replaced to-day by apparatus of a more scientific nature, it has been perhaps too readily forgotten.

Since Wedgwood, many have undertaken the measurement of high temperatures, but with varying success. Too indifferent to practical requirements, they have above all regarded the problem as a pretext for learned dissertations. The novelty and the originality of methods attracted them more than the precision of the results or the facility of the measurements. Also, up to the past few years, the confusion has been on the increase. The temperature of a steel kiln varied according to the different observers from 1500° to 2000° ; that of the sun from 1500° to $1,000,000^{\circ}$.

First of all, let us point out the chief difficulty of the problem. Temperature is not a measurable quantity in the strict sense of the term. To measure a length or a mass, is to count how many times it is necessary to take a given body chosen as a unit (meter, gramme) in order to obtain a complex system equivalent either as to length or mass of the body in question. The possibility of such a measurement presupposes the previous existence of two physical laws: that of equivalence, and that of addition. Temperature obeys well the first of these laws; two bodies in temperature equilibrium with a third, and thus equivalent with respect to exchanges of heat in comparison with this third body, will also be equivalent, that is to say, equally in equilibrium with respect to every other body which would be separately in equilibrium with one of them. This law allows determination of temperature by comparison with a substance arbitrarily chosen as a thermometric body. But the second law is wanting; one cannot, by the juxtaposition of several bodies at the same temperature, realize a system equivalent, from the point of view of exchanges of heat, to a body of different temperature; thus temperature is not measured, at least insomuch as one considers only the phenomena of convection.

In order to determine a temperature, one observes any phenomenon whatever varying with change of temperature. Thus for the mercury centigrade thermometer the temperature is defined by the *apparent expansion of mercury* from the *point of fusion of ice* measured by means of a unit equal to $\frac{1}{100}$ of the dilatation between the temperature of the *fusion of ice and that of the ebullition of water* under atmospheric pressure.

Thermometric Scales.—For such a determination there are four quantities to be chosen arbitrarily: the *phenomenon* measured, the thermometric *substance*, the *origin* of graduation, and the *unit* of measurement; while in a measurement properly so called there is but one quantity to be arbitrarily chosen, the magnitude selected as unity. It is evident that the number of thermometric scales may be indefinitely great; too often experimenters have considered it a matter of pride for each to have his own.

Here are some examples of thermometric scales chosen from among many:

Author.	Phenomenon.	Substance	Origin.	Unit.
Fahrenheit	Dilatation	Mercury	{ Very cold winter	{ 1/180 Ice to B. P.
Réaumur	"	"	Ice.....	1/80 " " "
Celsius	"	"	"	1/100 " " "
Wedgwood	{ Permanent contraction }	Clay	Dehydrated	1/2400 init. dimens.
Pouillet (Normal ther.)	Dilat. at const. p.	Air	Ice	
(Thermodyn. scale)	Dilat. at const. v.	Hydrogen	"	1/100
Siemens	{ Reversible heat-scale }	Anything	Heat=0	Ice to boiling-point
	Electric resistance	Platinum	Ice	

The enormous differences above mentioned in the measurements of high temperatures are much more the result of the diversity of the scales than due to the errors of the measurements themselves. Thus the experiments

on solar radiation which have led to values varying from 1500° to $1,000,000^{\circ}$ are based on measurements which do not differ among themselves by more than 25 per cent.

To escape from this confusion it was first necessary to agree upon a single scale of temperatures; that of the gas-thermometer is to-day universally adopted, and this choice may be considered as permanent. The gases possess, more than any other state of matter, a property very important for a thermometric substance—the possibility of being reproduced at any time and in any place identical with themselves; besides, their dilatation, which defines the scale of temperatures, is sufficient for very precise measurements; finally, this scale is practically identical with the thermodynamic scale. This last is in theory more important than all the other properties because it is independent of the nature of the phenomena and of the substances employed. It gives, too, a veritable measure and not a simple comparison; its only inconvenience is for the moment not to be experimentally realizable, at least rigorously, but it is impossible to say if this will always be the case.

The adoption of the scale of the gas-thermometer does not in any way imply the obligation to use this instrument actually in all measurements. Any thermometer may be taken, provided that in the first place its particular scale has been standardized by comparing it with that of the gas-thermometer. According to the case, there will be advantage in employing one or another method; practically also one almost never employs the gas-thermometer by reason of the difficulties inherent in its use, which result principally from its great dimensions and its fragility.

For the estimation of very high temperatures the gas-scale can be used only by an indirect extrapolation in terms of some property of matter whose variation has

been studied within the range of the gas-scale attainable experimentally and which variation is assumed to obey the same law at temperatures beyond which control cannot be had with the gas-thermometer.

The gas-scale has not been experimentally determined above 1150° C., and extrapolations to 1600° C. may be made by means of thermocouples made of the platinum metals, assuming the law connecting E.M.F. and temperature to be the same above 1150° C. as below. Beyond 1600° C. the most infusible substances permanently alter their properties and we are forced to measure temperature in terms of the radiations coming from heated bodies for the reason that we have not been able to find any other than the radiating properties of such excessively heated bodies whose variations can be measured without destroying or permanently altering either the substance used as pyrometer or the substance examined. Perhaps also chemical methods may be employed eventually.

It is in the realm of the laws of radiation and their applications to pyrometric methods that some of the most recent and important advances in high temperature measurements have been made, so that, with certain restrictions which will be treated in the chapter on the laws of radiation, it is possible to measure on a common scale the temperatures of bodies heated to the highest attainable limits.

It is our purpose, in this introduction, to pass in review rapidly the different pyrometric methods (that is to say, thermometers utilizable at high temperatures) whose employment may be advantageous in one or another circumstance; we shall then describe more in detail each of them, and shall discuss the conditions for their employment. But in the first place it is necessary to define within what limits the different scales may be compared to that of the normal gas-thermometer; it is the insufficiency

of this comparison which is still to-day the cause of the most important errors in the measurement of high temperatures.

Fixed Points.—The standardization of the different pyrometers is the most frequently made by means of the fixed points of fusion and ebullition which have been determined in the first place by means of the gas-thermometer; the actual precision of the measurements of high temperatures is entirely subordinate to that with which these fixed points are known; this precision was for a long time most unsatisfactory because these fixed points could only be determined in an indirect manner with the gas-thermometer, and some of them only by aid of processes of extrapolation, always very uncertain. Recent researches, however, by various observers, in which improved methods of heating have been used, as well as greater purity of materials and more carefully constructed and calibrated apparatus, have led to most concordant results, in the determination of fixed points, even by most varied methods.

Violle was the first to make a series of experiments of considerable precision, which up to the last few years were our only reliable data on the question. In a first series of researches he determined the specific heat of platinum by direct comparison with the air-thermometer between the temperatures of 500° and 1200°. He made use indirectly of the relation thus established between specific heat and temperature to determine by comparison with platinum the points of fusion of gold and silver; then, by extrapolation of this same relation, the points of fusion of palladium and of platinum.

Fusion.....	Ag	Au	Pd	Pt
	954°	1045°	1500°	1779°

Finally, in a second series of experiments, he deter-

mined by direct comparison with the air-thermometer the boiling-point of zinc.

Boiling-point.....	$\left\{ \begin{array}{l} \text{Zn} \\ 929.6 \end{array} \right.$
--------------------	---

Barus, chemist of the United States Geological Survey, has determined the boiling-points of several metals by means of thermoelectric couples standardized against the air-thermometer.

Boiling-point.....	$\left\{ \begin{array}{l} \text{Cd} \\ 772^\circ \text{ and } 784^\circ \end{array} \right.$	$\left\{ \begin{array}{l} \text{Zn} \\ 926^\circ \text{ and } 931^\circ \end{array} \right.$
Mean.....	778°	928°.5

Callendar and Griffiths, by means of a platinum resistance-thermometer calibrated up to 500° by comparison with the air-thermometer, have determined the following points of fusion and ebullition:

Fusion.....	$\left\{ \begin{array}{l} \text{Sn} \\ 232^\circ \end{array} \right.$	$\left\{ \begin{array}{l} \text{Bi} \\ 270^\circ \end{array} \right.$	$\left\{ \begin{array}{l} \text{Cd} \\ 322^\circ \end{array} \right.$	$\left\{ \begin{array}{l} \text{Pb} \\ 329^\circ \end{array} \right.$	$\left\{ \begin{array}{l} \text{Zn} \\ 421^\circ \end{array} \right.$
-------------	---	---	---	---	---

Boiling-point.....	$\left\{ \begin{array}{l} \text{Aniline} \\ 184^\circ.1 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Naphthaline} \\ 217^\circ.8 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Benzophenone} \\ 305^\circ.8 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Mercury} \\ 356^\circ.7 \end{array} \right.$	$\left\{ \begin{array}{l} \text{Sulphur} \\ 444^\circ.5 \end{array} \right.$
--------------------	--	--	---	--	--

These last figures may be compared with Regnault's, and Crafts' previous determinations:

Naphthaline	Benzophenone	Mercury	Sulphur
218°	306°.1	357°	445°

Heycock and Neville, employing the same method, but with extrapolation of the law of resistance for platinum established only up to 450°, have determined the following points of fusion:

Sn	Zn	Mg (99.5%)	Sb	Al (99%)	Ag	Au	Cu
232°	419°	633°	629°.5	654°.5	960°.5	1062°	1080°.5

At the Physikalische Reichsanstalt in Berlin, the question of establishing a temperature scale has received deserved attention. In the early nineties Holborn and

Wien, using a thermocouple calibrated in terms of a porcelain-bulb nitrogen-thermometer, found the fusing points:

Fusion.....	Ag	Au	Pd	Pt
	970°	1072°	1580°	1780°

With the possible exception of the Pt point these results were subsequently found to be all high by Holborn and Day, who worked with a platinum-iridium bulb nitrogen-thermometer and thermocouple, employing electric heating, two improvements that greatly increased the accuracy, and they unquestionably have obtained the results meriting the greatest confidence. Among others they determined the following:

Fusion.....	Cd	Zn	Sb	Al	Ag	Au	Cu
	321°.7	419°	630°.5	657°.5	961°.5	1064°	1084°

Mr. Daniel Berthelot, in a series of most skilfully executed investigations extending over several years, has recently calibrated thermocouples by comparison with a special form of gas-thermometer, making use of the variation of the index of refraction with density. He has in this way found the points:

Fusion.....	Ag	Au
	962°	1064°
Ebullition.....	Se	Cd
	690°	778°

Besides these primary measurements there are some very important secondary determinations, which will be discussed later. From all the results at hand we may conclude that the fixed points possessing the greatest reliability for the indirect standardization of the various thermometric scales and thus for the calibration of pyrometers are the following:

Fusion.....	Sn	Zn	Sb	Al	Ag	Au	Pt	Ir
	232°	419°	630°	657°	961°	1065°	1780°	2250°
Ebullition.....	Naphthaline	S	Cd	Zn				
	217°.9	444°.6	778°	925°				

We may consider the temperature scale as known with an accuracy better than:

0°.5	between	200°	and	500° C.
3	"	500	"	800
5	"	800	"	1100
25	"	1100	"	1600
50	above	1600		

A more detailed discussion of the determination of fixed points and their reliability and ease of reproduction will be found in Chapter XIII on Standardization.

Pyrometers.—There have been a great number of pyrometric methods proposed, among which we shall dwell only upon those which have had considerable use or promise to be useful.

Gas-pyrometer (Pouillet, Becquerel, Sainte-Claire-Deville, Barus, Chappuis, Holborn, Callendar).—Utilizes the measurement of change in pressure of a gaseous mass kept at constant volume. Its great volume and its fragility render it unsuitable for ordinary measurements; it serves only to give the definition of temperature and should only be used to standardize other pyrometers.

Calorimetric Pyrometer (Regnault, Violle, Le Chatelier, Siemens).—Utilizes the total heat of metals (platinum in the laboratory and nickel in industrial works). Is to be recommended for intermittent researches in industrial establishments because its employment demands almost no apprenticeship and because the cost of installation is not great.

Radiation-pyrometer (Rosetti, Langley, Boys, Rubens, Féry).—Utilizes the total heat radiated by warm bodies. Its indications are influenced by the variable emissive power of the different substances. Convenient for the evaluation of very high temperatures which no thermometric substance can withstand (electric arc, sun).

Optical Pyrometer (Becquerel, Le Chatelier, Wanner, Holborn-Kurlbaum, Morse).—Utilizes either the photometric measurement of radiation of a given wave-length of a definite portion of the visible spectrum, or the disappearance of a bright filament against an incandescent background. Its indications, as in the preceding case, are influenced by variations in emissive power. The intervention of the eye aids greatly the observations, but diminishes notably their precision. This method is mainly employed in industrial works for the determination of the temperatures of bodies difficult of access—for example, of bodies in movement (the casting of a metal, the hot metal passing to the rolling-mill).

Electric-resistance Pyrometer (Siemens, Callendar).—Utilizes the variations of electric resistance of metals (platinum) with the temperature. This method permits of very precise measurements, but requires the employment of fragile and cumbersome apparatus. It will merit the preference for very precise investigations in laboratories when we have a satisfactory determination of the variation of resistance of platinum in terms of the normal gas-thermometer. As a secondary instrument for the reproduction of a uniform temperature scale throughout the range in which the platinum resistance thermometer can be used, it is unsurpassed in precision and sensibility. It is also now constructed in convenient form for industrial use.

Thermoelectric Pyrometer (Becquerel, Barus, Le Chatelier).—Utilizes the measure of electromotive forces developed by the difference in temperature of two similar thermoelectric junctions opposed one to the other. In employing for this measurement a Deprez-d'Arsonval galvanometer with movable coil, one has an apparatus easy to handle and of a precision amply sufficient considering

the actual state of the means of standardization at our disposal in terms of the normal scale of temperature. This pyrometer, which has been used for a good many years in scientific laboratories, is rapidly spreading into general industrial use, where it renders most valuable service.

Contraction-pyrometer (Wedgwood).—Utilizes the permanent contraction that clayey materials take up when submitted to temperatures more or less high. It is employed to-day only in a few pottery works.

Fusible Cones (Seger).—Utilize the unequal fusibility of earthenware blocks of varied composition. Give only discontinuous indications. Such blocks studied by Seger are spaced so as to have fusing-points distant about 20°. In general use in pottery works and in some similar industries.

There are a number of other pyrometers which have been found suitable in special cases or which for one reason or another have been found convenient in some particular line of work. Some of these we shall mention, among them being the meldometer (Joly), interesting to the chemist or metallurgist for determining fusing temperatures of minute specimens; the various industrial instruments based on the relative expansion of metals or of a metal and graphite used in air-blasts and metal baths; and finally pyrometers based on the flow of air or vapor (Hobson, Uhling-Steinbart, Job).

CHAPTER I.

NORMAL SCALE OF TEMPERATURES.

WE have seen that temperature is not a measurable quantity; it is merely comparable with respect to a scale arbitrarily chosen.

The normal scale is the *thermodynamic scale*; but as it is impossible to realize rigorously this scale, it is necessary to have a practical one. In the same way that, besides the theoretical definition of the meter, there is a practical standard, a certain meter kept at the Bureau International des Poids et Mesures, there exists, besides the normal scale of temperatures, a practical scale which is a certain gas-thermometer which we are going to study.

Laws of Mariotte and Gay-Lussac.—The laws of Mariotte and Gay-Lussac are the basis for the use of the dilatation of gases for the determination of temperatures. These two laws may be written

$$\frac{p_1 v_1}{p_0 v_0} = \frac{1 + \alpha t_1}{1 + \alpha t_0}, \dots \dots \dots \quad (1)$$

the temperatures being measured with the mercury-thermometer. α is a numerical coefficient, the same for all gases, at least to a first approximation, and its value is

$$\alpha = 0.00366 = \frac{1}{273}$$

when it is agreed that the interval between the temperatures of melting ice and boiling water is 100°.

But instead of considering the formula (1) as the expression of an experimental law joining the product pv to the temperature defined by the mercury-thermometer, we may require of experiment merely the law of Mariotte and write *à priori* the formula in question, giving a new definition of temperature approximating that of the mercury-thermometer. This new scale has the advantage that it adapts itself to the study of very much higher temperatures. The use of this process suggested by Pouillet was carefully studied by Regnault.

The expression for the laws of Mariotte and Gay-Lussac can be put in the form

$$pv = nR \left(\frac{1}{\alpha} + t \right) \dots \dots \dots \quad (2)$$

by calling n the number of units of quantity (this unit may be either the molecular weight or the gramme); R the value of the expression

$$\frac{p_0 v_0}{\frac{1}{\alpha} + t_0}$$

for unit quantity of matter taken at the temperature of melting ice and under atmospheric pressure.

Gas-thermometers.—The equivalent expressions (1) and (2) which arbitrarily by convention give the definition of temperature, can be utilized, from the experimental point of view, in various ways for the realization of the normal thermometer.

1. *Constant-volume Thermometer.*—In the thermometer designated by this name, the volume and the mass are kept invariable.

The expression (2) then gives between the two temperatures t and t_0 the relation

$$\frac{p}{p_0} = \frac{1}{\alpha} + t_0,$$

from which

$$t - t_0 = p - p_0 \left(\frac{1}{\alpha} + t_0 \right) \dots \dots \dots \quad (3)$$

2. *Constant-pressure Thermometer*.—In this case the pressure and the volume of the heated mass remain constant, but the mass is variable; a part of the gas leaves the reservoir. The expression (2) then gives

$$1 = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{n_0 - n}{n_0} \left(\frac{1}{\alpha} + t \right) \dots \dots \dots \quad (4)$$

It would be much more logical, instead of the classic expressions constant-volume thermometer or constant-pressure thermometer, to say *thermometer of variable pressure*, *thermometer of variable mass*, which describe much more exactly the manner of their action.

3. *Thermometer of Variable Pressure and Mass*.—The action of this apparatus combines those of the two preceding types. A part of the gas leaves the reservoir, and the pressure is not kept constant. The expression (2) gives

$$\frac{p}{p_0} = \frac{n}{n_0} \cdot \frac{\frac{1}{\alpha} + t}{\frac{1}{\alpha} + t_0},$$

from which

$$t - t_0 = \frac{p n_0 - p_0 n}{p_0 n} \cdot \left(\frac{1}{\alpha} + t_0 \right). \dots \dots \quad (5)$$

4. *Volumetric Thermometer*.—There exists a fourth method of the use of the gas-thermometer which was suggested by Ed. Becquerel, and presents, as we shall see later, a particular interest for the evaluation of high temperatures. We keep the name for it given by its inventor. The determination of the temperature is obtained by two measurements made at the same temperature, and not as in the preceding methods by two measurements made at two different temperatures one of which is supposed known. The mass contained in the reservoir is varied, and the ensuing change of pressure is observed. The expression (2) gives

$$p v = n R \left(\frac{1}{\alpha} + t \right),$$

$$p' v = n' R \left(\frac{1}{\alpha} + t \right),$$

from which

$$(p - p') v = (n - n') R \left(\frac{1}{\alpha} + t \right),$$

or

$$t = -\frac{1}{\alpha} + \frac{p - p'}{n - n'} \cdot \frac{v}{R}. \dots \dots \quad (6)$$

This necessitates a preliminary determination of the constant R .

In the particular case in which $p' = 0$, which supposes that a complete vacuum is obtained, the preceding relation becomes simpler and is

$$t = -\frac{1}{\alpha} + \frac{p}{n} \cdot \frac{v}{R}. \dots \dots \quad (7)$$

The definitions of temperature given by these different thermometers would be equivalent among themselves and with that of the mercury-thermometer if the laws of Mariotte and Gay-Lussac were rigorously exact, as used to be held. The only advantage of the gas-thermometer in that case would be to extend to high temperatures the scale of the mercury-thermometer. In this way it was employed by Pouillet, Becquerel, Sainte-Claire-Deville.

Experiments of Regnault.—The very precise experiments of Regnault caused a modification in the then admitted ideas concerning the mercury-thermometer as well as the gas-thermometer, and have led to the definite adoption of a normal gas-thermometer.

In the first place these experiments established that different mercury-thermometers are not comparable among themselves on account of the unequal dilatation of the differing glass employed in their construction. Thus they cannot give an invariable scale for the determination of temperature. In comparing them from 0° to 100° they do not present between these extreme temperatures very great differences, 0°.30 as a maximum, but at temperatures above 100° these differences may become considerable and reach 10.°

Constant-vol. Air-thermometer, $p_0 = 760.$	Mercury-thermometer in			
	Crystal.	White Glass.	Green Glass.	Bohemian Glass.
100°	+ 0°.00	+ 0°.00	+ 0°.00	+ 0°.00
150	+ 0 .40	- 0 .20	+ 0 .30	+ 0 .15
200	+ 1 .25	- 0 .30	+ 0 .80	+ 0 .50
250	+ 3 .00	+ 0 .05	+ 1 .85	+ 1 .44
300	+ 5 .72	+ 1 .08	+ 3 .50	
350	+10 .50	+ 4 .00		

The numbers figuring in this table indicate the quantities by which it is necessary to increase or diminish the temperatures given by the air-thermometer in order to have them correspond with those which were observed with the different mercury-thermometers.

It was thus impossible to define the practical scale of temperatures in terms of the mercury-thermometer. The use of the gas-thermometer became necessary. But Regnault recognized that it was not possible to take a *single coefficient of dilatation* α , independent of the *nature* of the gas, of its *pressure*, and of the *mode of dilatation* utilized. The coefficient of expansion at constant volume (α) and the coefficient of expansion at constant pressure (β) are not identical. This follows from the fact that the law of Mariotte is not rigorously exact; we have in reality

$$pv = p_0 v_0 + \epsilon,$$

ϵ being a very small quantity, but not zero.

The experiments of Regnault permitted him not only to detect but to measure this variation of the coefficient of expansion. Here are, for example, the results which he found for air between 0° and 100° :

Volume Constant.			Pressure Constant.		
Pressure.	α	$\frac{1}{\alpha}$	Pressure.	β	$\frac{1}{\beta}$
266	0.003656	273.6	760	0.003671	272.4
760	3655	272.8	2525	3694	270.7
1692	3689	271	2620	3696	270.4
3655	3709	269.5			

For air at $4^\circ.5$ Rankine obtains, from the experiments of Regnault, the formula

$$pv = p_0 v_0 + 0.008163 \frac{p - p_0}{\omega} \cdot pv,$$

ω being the atmospheric pressure.

These coefficients vary also from one gas to another, as is shown by the following table, taken also from Regnault's experiments:

MEAN COEFFICIENT BETWEEN 0° AND 100°.

Volume Constant.			Pressure Constant.		
Pressure. mm.	α	$\frac{1}{\alpha}$	Pressure. mm.	β	$\frac{1}{\beta}$
AIR.					
760	0.003665	272.8	760	0.003671	272.4
3655	3708	269.5	2620	3696	270.4
HYDROGEN.					
760	3667	272.7	760	36613	273.1
			2545	36616	273.2
CARBON MONOXIDE.					
760	3667	272.7	760	3669	272.5
NITROGEN.					
760	3668	272.6			
CARBONIC ACID.					
760	3688	271.2	760	3710	296.5
3589	3860	259	2520	3845	259.5
SULPHUROUS ACID.					
760	3845	259.5	760	3902	253.0
			980	3980	251.3

These experiments show that the easily liquefiable gases have coefficients quite different from those of the permanent gases.

For the permanent gases the coefficients for constant volume differ much less among themselves than those for constant pressure; for the former the extreme deviation does not exceed $\frac{1}{1000}$; for the latter it is three times as great. Setting aside air, which is a mixture and which contains more easily liquefiable oxygen, the coefficients for constant volume of H_2 , N_2 , and CO are identical.

Finally, for hydrogen the coefficient of expansion does not vary with the pressure.

The inequality of the coefficients of expansion, however, does not prevent us from taking any gas whatever to define the scale of temperature, provided we apply to it the proper coefficient determined by experiment between 0° and 100° . The scales are identical, if the coefficients of expansion do not vary with the temperature. This is the conclusion to which Regnault came from a comparison of thermometers at constant volume, differing by their initial pressure or the nature of the gas. Here are the results obtained, starting from the fixed points 0° and 100° , by the aid of the following formulæ:

$$\begin{aligned}pv &= nRT, \\p_0v &= nRT_0, \\p_{100}v &= nRT_{100}, \\ \frac{p-p_0}{p_{100}-p_0} &= \frac{T-T_0}{T_{100}-T_0} = \frac{t}{100}.\end{aligned}$$

AIR-THERMOMETER.

$p_0 = 751$ mm.	$p_0 = 1486$ mm.
Degrees.	Degrees.
156.18	156.19
259.50	259.41
324.33	324.20

PRESSURE = 760 MILLIMETERS.

Air-thermometer.	Hydrogen-thermometer.	Air-thermometer.	CO_2 -thermometer.
Degrees.	Degrees.	Degrees.	Degrees.
141.75	141.91	159.78	160.00
228.87	228.88	267.35	267.45
325.40	325.21	322.8	322.9

The deviations do not exceed $0^{\circ}.2$, a value that Regnault estimated not to exceed the limits of error of his experiments; he concluded from this that one gas may be used as well as another, and he took air for the normal thermometer.

Nevertheless his experiments on sulphurous acid had shown a very marked variation of the coefficient of expansion of this gas with the temperature. The following table gives the mean coefficient at constant volume between 0° and t° :

t	α
98.0	0.0038251
102.45.	38225
185.42.	37999
257.17.	37923
299.90.	37913
310.31.	37893

By analogy it is permissible to suppose that a similar effect should take place with the other gases; but the differences were then too small, and the degree of precision of the methods of Regnault insufficient to detect it.

Results Obtained by Chappuis.—This effect has been demonstrated by experiments of very great precision made at the Bureau International des Poids et Mesures, at Sèvres. Chappuis has found, between 0° and 100° , systematic deviations between thermometers of hydrogen, nitrogen, and carbonic acid, filled at 0° under a pressure of 1000 mm. of mercury.

Hydrogen Ther.	N Ther.—H Ther.	N Ther.—CO ₂ Ther.
— 15°	—0°.016	—0°.094
0	0	0
+ 25	+0 .011	+0 .050
+ 50	+0 .009	+0. 059
+ 75	+0 .011	+0 .038
+100	0	0

In this table, taking as definition of the temperature the hydrogen-thermometer at constant volume, the numbers in the last two columns indicate the deviations observed with the thermometers of nitrogen and carbonic acid; it is certain that these deviations are systematic. These results allow of the determination of the mean coefficients of expansion:

t	α (Hydrogen)	α (Nitrogen).	α (Carbonic Acid).
0°	0.00367689	0.00373538
100°	0.00366254	367466	372477

Thus the coefficients decrease with rise of temperature, while remaining higher than that of hydrogen, to which they tend to approach. The more recent work of Chappuis and Harker and others in the establishment of a normal scale of temperatures for high temperatures will be discussed in the following sections.

In the interval 0°—100°, the values given above, calculated from Chappuis' data of 1888, may not be absolutely

DIFFERENCE BETWEEN SCALES OF NITROGEN- AND HYDROGEN-THERMOMETERS.

$$t_n - t_h. \text{ vol.} = \text{const.}, \quad P_0 = 100 \text{ cms.}$$

Temp. Cent.	Callendar. 1903.	Chappuis. 1902.	Rose-Innes. 1901.	Lehfeldt. 1898.
+20	+.006	+.005	+.002	+.011
+40	+.009	+.003	+.002	+.017
+50	+.009	+.010	+.002	+.019
+60	+.008	+.009	+.002	+.019
+80	+.005	+.004	+.001	+.015

exact, but they are probably very nearly correct. Some of the later results are given below; those marked Cal-
lendar are calculated by him from the data of Kelvin and Joule using a modified formula; Chappuis' results are from his latest determinations (1902) while those of Lehrfeldt and Rose-Innes are calculations involving special thermodynamical assumptions.

Normal Scale of Temperatures.—It results from these experiments that the different scales furnished by the various gas-thermometers are not rigorously identical; the deviations between 0° and 100° are very small, but their existence is certain. It becomes necessary, therefore, in order to have a *scale of temperature rigorously defined*, to make a choice of the *nature* of the gas, of its *manner of dilatation*, and of its initial *pressure*.

The *normal thermometer* selected by the Bureau International des Poids et Mesures to define the practical scale of temperatures, and everywhere adopted to-day, is the *hydrogen thermometer*, operated at constant volume and filled with gas at 1000 millimeters of mercury at the temperature of melting ice.

For high temperatures this definition is inadmissible, because we would reach such pressures that the apparatus could not withstand. The use of the method at constant volume, that is to say, at invariable mass, is besides bad on account of the permeability of the coverings at high temperatures. It would be of great advantage to be able to employ a gas other than hydrogen and operate the thermometer at variable mass.

In the actual state of experimentation at high temperatures, it is impossible to have results exact to about 1° , and indeed, practically, we are far from arriving at this precision. It is very likely that we can, under these conditions, employ indifferently for the construction of the

normal thermometer any permanent gas whatsoever. According to the preceding experiments, all the gases would have a dilatation slightly greater than that for hydrogen, and their coefficient of expansion, which decreases with rise of temperature, would approach that for hydrogen. For determining experimentally the error possible with a normal thermometer thus modified, we possess actually but little data.

Crafts has compared in the neighborhood of 1500° the expansion at constant pressure of nitrogen and carbonic acid, and found for this latter the mean coefficient 0.00368 in assuming 0.00367 for nitrogen.

The experiments were made by displacing in a Meyer's tube nitrogen by carbonic acid, or carbonic acid by nitrogen.

10 cc. N ₂ displace	10 cc. CO ₂ displace
10.03 of CO ₂	9.95 of N ₂
10.01	9.91
10.00	9.98
10.03	9.93
9.95	—
10.09	Mean 9.94
Mean 10.02	

The two measurements give positive and negative differences of the same order of magnitude; but it should be noticed that the observed deviation ($\frac{4}{1000}$ on an average) hardly exceeds the possible error of observation. However it may be, carbonic acid, which differs much from the permanent gases at ordinary temperatures, no longer so differs in an appreciable degree at 1500°.

Violle has made some comparative measurements on the air-pyrometer used at constant pressure and constant

volume in his determinations of the specific heat of platinum.

Vol. Constant.	Press Constant.	Difference.
1171°	1165°	6°
1169	1166	3
1195	1192	3

There was on an average a deviation of only 4° between the two modes of observation, and the greater part of this deviation should be laid to accidental variations of the gaseous mass resulting from the permeability of the coverings.

Chappuis has made an exhaustive experimental study of the divergences of gases from the normal scale, and he finds that the coefficient of nitrogen (at const. vol.) gradually diminishes as above stated (p. 21), but that at about 75° C. it reaches a limiting value equal to

$$\alpha_{\lim} = 0.00367380$$

and it may be assumed that above this temperature the gas is in a perfect state.

The mean coefficient at constant volume for this gas between 0° and 100° is

$$\alpha_{0-100} = 0.00367466$$

and the limiting value for an initial pressure $P_0 = 0$ is

$$\alpha_{P_0=0} = 0.0036613.$$

This follows from the divergence that Chappuis and Harker found for the constant-volume nitrogen-thermometer from the normal scale of temperatures, in terms of the initial pressure; their experiments gave

$$\frac{\delta \alpha}{\delta p} = 1.32 \cdot 10^{-8} \text{ per mm. change in pressure,}$$

Such a normal scale of temperature for the nitrogen-thermometer is given by finding the coefficient α , at 0° C. for a pressure P'_0 which the gas would have supposing it to remain perfect in the range $0-100$. If $P_0 = 100$ cm., $P_{100} = 136.7466$ cm., whence $P'_0 = 100.0086$ and $\alpha = \frac{P_{100} - P'_0}{100P'_0} = 0.00367348$ if $\alpha_{\text{lim}} = 0.00367330$ as stated above.

Nitrogen at constant pressure gives

$$\frac{\delta\beta}{\delta p} = 1.19 \cdot 10^{-8} \text{ per mm.}$$

and $\beta_{\text{lim}} = 0.0036612$.

The divergences from the normal scale in this case are about double those at constant volume, and the divergences between the uncorrected scale and the theoretical scale of the constant-volume thermometer whose constants are given above and which represents the normal scale of temperatures, are proportional to the temperature measured from 100° and have the following values:

At 100°	$0^\circ.000$
200023
300047
400070

These deviations are evidently very slight and are entirely negligible within this range for practically all pyrometric uses. We shall see, however, that at 1000° this correction may assume a certain importance.

For hydrogen, the limiting values given by D. Berthelot are:

$$\alpha_{\text{lim}} = 0.0036625,$$

$$\beta_{\text{lim}} = 0.0036624,$$

and the deviations of this gas from the normal scale are immaterial.

The experiments of Chappuis and Harker were carried out at the International Bureau of Weights and Measures and included a comparison of the platinum-resistance and nitrogen-thermometers up to 500° C. and a determination of the sulphur boiling-point, to which questions we shall return.

We can then affirm that, in employing any permanent gas with any mode of dilatation, we shall not differ certainly by more than 5° at 1000° from the temperature of the normal scale, and in reality the deviation will be without doubt much less, and should not reach 1°.

Theoretically it would be preferable to use hydrogen under reduced pressure, which would certainly not give deviations of 1° from the normal scale; but there is always the danger of the passage of this gas through the coverings, and of its combustion by oxygen or oxides.

Practically it would be better to take nitrogen, whose expansion deviates little from that of hydrogen, less than the deviation of air. Callendar has suggested the use of helium or one of the other newly discovered inert, monatomic gases, as they diverge less than nitrogen from the hydrogen scale, cannot dissociate and do not pass through metals.

For high temperatures the normal thermometer will be, then, one of nitrogen or other inert gas.

Thermodynamic Scale.—It is defined, in terms of Carnot's principle applied to a reversible cycle working between two sources at constant temperatures, by the relation

$$\frac{Q_1}{Q_0} = \frac{T_1}{T_0} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (1)$$

1. Approximate Expression.—Consider Carnot's cycle formed, as is well known, of two isotherms and two adia-

batics, and let us seek the quantity of heat absorbed following the isotherm T_1 .

From Joule's experiments we have approximately

$$Q_1 = A \int pdv.$$

The laws of Mariotte and Gay-Lussac give

$$pv = R \left(\frac{1}{\alpha} + t \right),$$

where t is the temperature of the gas-thermometer; then,

$$dv = -R \frac{dp}{p^2} \left(\frac{1}{\alpha} + t \right); \text{ and}$$

$$Q_1 = -AR \left(\frac{1}{\alpha} + t_1 \right) \cdot \int_{p_1'}^{p_1''} \frac{dp}{p} = AR \left(\frac{1}{\alpha} + t \right) \log \frac{p_1'}{p_1''}.$$

Similarly,

$$Q_0 = AR \left(\frac{1}{\alpha} + t_0 \right) \log \frac{p_0'}{p_0''}.$$

Equation (1) becomes

$$\frac{T_1}{T_0} = \frac{Q_1}{Q_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0} \left(\log \frac{p_1'}{p_1''} - \log \frac{p_0'}{p_0''} \right) \dots \dots \quad (2)$$

But the experiments on adiabatic expansion give

$$pv^r = \text{const.},$$

and combining with the laws of Mariotte and Gay-Lussac,

$$p^{r-1} \cdot t^{-r} = \text{const.}$$

Consequently $\frac{p_1}{p_0}$ depends only on the ratio $\frac{t_1}{t_0}$, which is the same the whole length of the two isotherms. Thus

$$\frac{p_1'}{p_0'} = \frac{p_1''}{p_0''},$$

or

$$\frac{p_1'}{p_1''} = \frac{p_0'}{p_0''}.$$

Equation (2) then takes the very simple form

$$\frac{T_1}{T_0} = \frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0};$$

that is to say, the *ratio of the absolute thermodynamic temperatures is equal to the ratio of the absolute temperatures of the gas-thermometer*; and if in the two scales it is agreed to take equal to 100 the interval comprised between the temperatures of melting ice and the vapor of boiling water, we have, at any temperature, the equality

$$T = \frac{1}{\alpha} + t.$$

But this is only a first approximation, for we have employed relations that are but roughly so: the laws of Joule, Mariotte, and Gay-Lussac.

2. Reconsider the problem by a more exact method.

Since T differs very little from $\frac{1}{\alpha+t}$, and since the laws

of Mariotte and Gay-Lussac are nearly true, we place, following a method of calculation indicated by Callendar,

$$pv = RT(1 - \phi),$$

ϕ being a very small function of p and of T (thermodynamic temperature).

We have then, between the temperature of the gas-thermometer and the thermodynamic temperature, the relation

$$\frac{\frac{1}{\alpha} + t_1}{\frac{1}{\alpha} + t_0} = \frac{T_1(1 - \phi_1)}{T_0(1 - \phi_0)},$$

which will permit of passing from one scale of temperature to the other if we know the corresponding value of ϕ .

Consider, as before, Carnot's cycle, and let us determine the heat of isothermal expansion in a more exact manner, by utilizing the experiments of Joule and Thomson on the expansion through a porous plug, and those of Regnault on the deviations from Mariotte's law.

We write for this that the changes in energy between two given isothermal states are the same, either for the reversible expansion or for the expansion of Joule and Thomson.

$$Q_1 - A \int_{p_1'}^{p_1''} pdv = -A(p_1''v_1'' - p_1'v_1') + \int_{p_0'}^{p_1''} \frac{d\varepsilon_1}{dp} dp,$$

ε being the very feeble change in heat of the gas accompanying its passage through the porous plug, in the experiment of Joule and Thomson. We get from this

$$Q_1 = A \int_{p_1'}^{p_1''} vdp + \int \frac{d\varepsilon_1}{dp} dp \text{ (at constant temperature)}, \quad (3)$$

for

$$d(pv) = pdv + vdp.$$

The relation

$$pv = RT(1 - \phi)$$

gives for the value of v

$$v = \frac{RT}{p}(1 - \phi),$$

which, substituted in equation (3), leads to

$$Q_1 = ART_1 \cdot \int_{p_1'}^{p_1''} \frac{dp}{p} - ART_1 \cdot \int \phi_1 \frac{dp}{p} + \int \frac{d\epsilon_1}{dp} dp. \quad (4)$$

Similarly, we have

$$Q_0 = ART_0 \cdot \int_{p_0'}^{p_0''} \frac{dp}{p} - ART_0 \cdot \int \phi_0 \frac{dp}{p} + \int \frac{d\epsilon_0}{dp} dp. \quad (5)$$

If we introduce these values in the expression for Carnot's cycle, after division by T_1 and T_0 we should find an identity:

$$\begin{aligned} \frac{Q_1}{T_1} - \frac{Q_0}{T_0} &= AR \log_e \frac{p_1'' p_0'}{p_1' p_0''} - \int_{p_1'}^{p_1''} \left(AR \frac{\phi_1}{p} - \frac{1}{T_1} \cdot \frac{d\epsilon_1}{dp} \right) dp \\ &\quad + \int_{p_0'}^{p_0''} \left(AR \frac{\phi_0}{p} - \frac{1}{T_0} \cdot \frac{d\epsilon_0}{dp} \right) dp = 0. \end{aligned}$$

The law of adiabatic expansion gives

$$\frac{p_1'' p_0'}{p_1' p_0''} = 1 \quad \log_e \frac{p_1'' p_0'}{p_1' p_0''} = 0.$$

In order, then, that the expression reduce to an identity it is necessary that

$$\frac{1}{T} \cdot \frac{d\epsilon}{dp} = AR \frac{\phi}{p}, \quad \text{or} \quad \phi = \frac{d\epsilon}{dp} \cdot p \cdot \frac{1}{AR} \cdot \frac{1}{T}.$$

Referring to the experiments on air of Joule and Thomson, we have

$$\phi = 0.001173 \cdot \frac{p_1}{p_0} \cdot \left(\frac{T_0}{T_1} \right)^{\frac{3}{2}},$$

p_0 being the atmospheric pressure, and T_0 the temperature of melting ice.

This is still an approximate result, for we have depended upon the experiments of Joule and Thomson and on the law of adiabatic expansion; however, the approximation is more close. If it seems sufficient for air, it is certainly not so for carbonic acid. Neither is the formula rigorously exact for air.

Callendar has calculated the correction to make to the air-thermometer readings by extrapolation up to 1000°, and he found the following results:

Readings of Centigrade Thermometer.	Volume Constant.		Pressure Constant.	
	ϕ	Δt	ϕ	Δt
0°	0.001173	0	0.001173	0
100	0.000627	0	0.000457	0
200	393	0.04	225	0.084
300	267	0.09	127	0.20
500	147	0.23	52	0.47
1000	54	0.62	12	1.19

The deviations of the air-thermometer at high temperatures are thus very slight if concordance is established at 0° and 100° and we have seen that in the case of nitrogen the experiments of Chappuis and Harker have shown the same to be true for this gas. In an experimental investigation, not yet completed, on the dilatations of nitrogen, air, oxygen, carbon monoxide and carbonic acid throughout the range 0°—1000° Jacquerod and Perrot find, using a quartz bulb at constant volume, that the coefficients of the first three remain excessively close together throughout this range and that the coefficient for carbonic acid, although less than in the 0°—100°

interval, remains considerably greater than for the other gases.

Callendar, in a recent computation based upon the work of Kelvin and Joule and the experiments of Chappuis and others, arrives at the following values for the scale corrections for the best thermometric gases:

SCALE CORRECTIONS FOR GASES, ASSUMING $\theta_0 = 273^{\circ}.10$.

Temp. Cent.	Constant Pressure, 76 cms.				Constant Volume $p_1 = 100$ cms.			
	Helium.	Hydro- gen	Nitro- gen.	Air.	Helium.	Hydro- gen.	Nitro- gen.	Air.
- 150	+0.073	+0.084	+0.945	+0.901	-0.026	+0.013	+0.195	+0.186
- 100	+ .030	+ .022	+ .328	+ .314	- .012	+ .005	+ .080	+ .076
- 50	+ .009	+ .006	+ .090	+ .086	- .004	+ .002	+ .024	+ .023
- 20	+ .003	+ .002	+ .025	+ .024	- .001	+ .000	+ .007	+ .007
+ 20	- .0016	- .0009	- .0141	- .0134	+ .0008	- .0003	- .0043	+ .0041
+ 40	- .0022	- .0013	- .0195	- .0186	+ .0011	- .0004	- .0059	+ .0056
+ 50	- .0022	- .0013	- .0195	- .0186	+ .0011	- .0004	- .0059	+ .0056
+ 60	- .0021	- .0012	- .0180	- .0172	+ .0011	- .0004	- .0054	+ .0053
+ 80	- .0013	- .0008	- .0113	- .0108	+ .0007	- .0002	- .0038	+ .0034
+ 150	+ .0054	+ .0029	+ .043	+ .041	- .0031	+ .0010	+ .0143	+ .0136
+ 200	+ .0128	+ .0068	+ .101	+ .096	- .0076	+ .0024	+ .035	+ .033
+ 300	+ .0332	+ .0165	+ .243	+ .232	- .203	+ .0059	+ .088	+ .084
+ 450	+ .071	+ .034	+ .495	+ .472	- .047	+ .013	+ .189	+ .180
+ 1000	+ .243	+ .104	+ 1.53	+ 1.46	- .187	+ .044	+ .646	+ .616

The above table indicates that for the gases hydrogen and helium no attention need be paid to the thermodynamic correction, for it is quite negligible for the whole temperature range for these two gases. All the gases are also seen to have a greater correction at constant pressure than at constant volume. Again it is to be noted that at small initial pressures these corrections will be proportionally reduced, and finally that it is only in the most refined work that this correction need be applied, as in the establishment of a fixed point in pyrometry as the gold fusing-point.

D. Berthelot has indicated a simple method for calculating this thermodynamic correction for any gas.

For a constant volume thermometer:

$$T - T_0 = t \left(1 - \frac{a}{373} \frac{100-t}{273+t} \right),$$

T_0 being the absolute temperature of melting ice (273°.10), T the absolute temperature sought corresponding to the centigrade temperature t given by the gas-thermometer in question at an initial pressure p the correction to t must be multiplied by $\frac{p}{76}$.

For the constant-pressure thermometer

$$T - T_0 = t \left[1 - \frac{a}{373} \frac{100-t}{273+t} \left(1 + \frac{273}{373} \frac{646+t}{273+t} \right) \right].$$

The value of a depends upon the critical constants of the gas and is

$$a = \frac{27}{64} R^2 \cdot \frac{T_c^3}{p_c},$$

where R is the gas constant (here $\frac{1}{273.1}$), T_c and p_c the critical pressure and temperature respectively.

TABLE OF CRITICAL CONSTANTS.

	p_c	t_c	a
Carbonic acid.....	72.9 atm.	+ 31.3	2.188
Oxygen.....	50.0	-118	0.422
Air.....	39.0	-140	.342
Carbon monoxide.....	35.9	-141	.363
Nitrogen.....	33.6	-146	.343
Hydrogen.....	13.0	-240	.016
Helium.....	?	?	(small)

The formulae of Berthelot give practically identical values for the thermodynamic corrections as found by Callendar. Experimental science has now reached such a development that as above stated these corrections cannot always be neglected. It is to be noted in confirmation of this statement that the sulphur boiling-point as determined by Callendar and Griffiths in terms of a constant-pressure thermometer was $0^{\circ}.2$ lower than found by Chappuis and Harker on the constant-volume scale, a difference practically identical with that indicated by the above table.

The experiments of Kelvin and Joule may also be used to determine the absolute temperature of the point of fusion of ice on the thermodynamic scale. Below are the results of a computation by Lehrfeldt:

	Gas-ther.	Thermodyn.	Ther.
Hydrogen	273°.08	272°.8	
Air.....	272 .43	273 .27	
Nitrogen.....	273 .13	273 .2	
Carbonic acid.	268 .47	{ 274 .83 (Thomson) 273 .48 (Natanson)	

The thermodynamic temperature of melting ice should be in all cases the same; the deviations come mainly from the uncertainties in the measurements of the heat of expansion, indicating the desirability of repeating Joule and Thomson's work with modern appliances.

A later calculation by Rose-Innes based on the recent work of Chappuis shows that there is still an outstanding difference of $0^{\circ}.08$ in the absolute temperature of melting ice as given by hydrogen and nitrogen and suggests that this might be accounted for by occlusion on a very small scale. Further experimental evidence on this point is needed and the absolute value of the ice-point is still

uncertain by over $0^{\circ}.1$. The following table gives Callendar's résumé of the expansive properties of the thermometric gases. In the table θ_0 is the thermodynamic temperature of the ice-point as determined from hydrogen, and T_0 this point on the various gas-scales.

EXPANSION AND PRESSURE COEFFICIENTS FOR $\theta_0 = 273^{\circ}.10$.

Gas.	Constant Pressure 76 cm.			Constant Volume $p_0 = 100$ cm.		
	$\theta_0 - T_0$	T_0	$1/T_0$	$\theta_0 - T_0$	T_0	$1/T_0$
Helium....	+ 0.10	273.00	.0036628	+ 0.19	272.91	.0036640
Hydrogen..	- .135	273.235	.00365985	+ .067	273.034	.00366254
Nitrogen...	+ .70	272.40	.0036708	+ .99	272.11	.00367466
Air.....	+ .71	272.39	.0036709	+ .96	272.14	.00367425

CHAPTER II.

NORMAL THERMOMETER.

Sèvres Thermometer.—This thermometer is a constant-volume thermometer filled with pure, dry hydrogen, under the pressure of 1 m. of mercury at the temperature of melting ice. It consists of two essential parts: the *reservoir*, enclosing the invariable gaseous mass, and the *manometer*, serving to measure the pressure of this gaseous mass.

The *reservoir* is made of a platinum-iridium tube whose volume is 1.03899 liters at the temperature of melting ice. Its length is 1.10 m., and its outer diameter 0.036 m. It

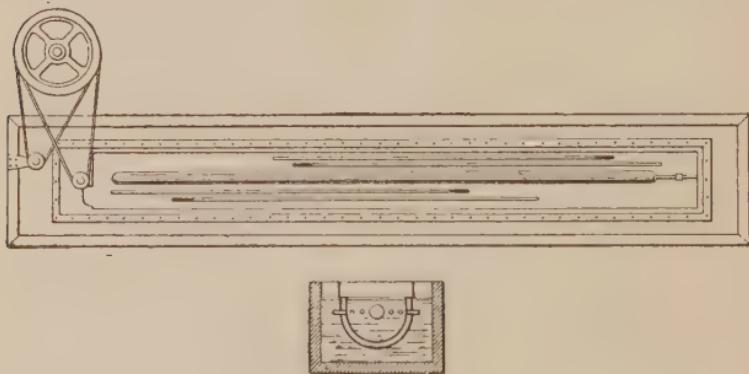


FIG. 1.

is attached to the manometer by a capillary tube of platinum of 0.7 mm. diameter. This is as small as is safe to make this tube on account of the otherwise too slow establishment of pressure equilibrium.

This reservoir is supported horizontally in a double box with interior water circulation. For the determination of the 100° mark, indispensable for standardization, the reservoir can be placed in the same way in a horizontal heater supplied with steam and composed of several concentric coverings.

Manometer. — The manometric apparatus is mounted upon an iron support of 2.10 m. height, which is made of a railway rail firmly bolted to a tripod of wrought iron. The lateral parts attached to this rail, planed their entire length, carry sliding pieces to which are fastened the manometer tubes and a barometer. Fig. 2 represents, in a slightly modified form, the manometric apparatus. It is composed essentially of a manometer open to the air whose open arm serves as cistern for a barometer. The other arm, closed half-way up by a piece of steel, is attached to the thermometric reservoir by the capillary tube of platinum. The two manometer tubes, each of 25 mm. interior diameter, have their lower ends fixed into a block of steel. They communicate with each other by holes of 5 mm. diameter bored in the block. A stop-cock permits closing this connection. A second three-way cock is screwed on the same block. One of its branches can serve to let mercury run out; the other, to which is attached a long flexible steel tube, puts the manometer in communication with a large reservoir of mercury which can be raised or lowered the length of the support, either rapidly by hand, or slow-motioned by means of a screw.

The barometer which sets in the open branch is fixed at its upper part on a carriage whose vertical displacement is regulated throughout a length of 0.70 m. by a strong screw. The latter is held at its two ends by two nuts which permit it to turn without longitudinal motion; it

works in a screw attached to the carriage, and carries at its lower end a toothed pinion which works into a cog-wheel. It suffices to turn this wheel by acting upon the rod which

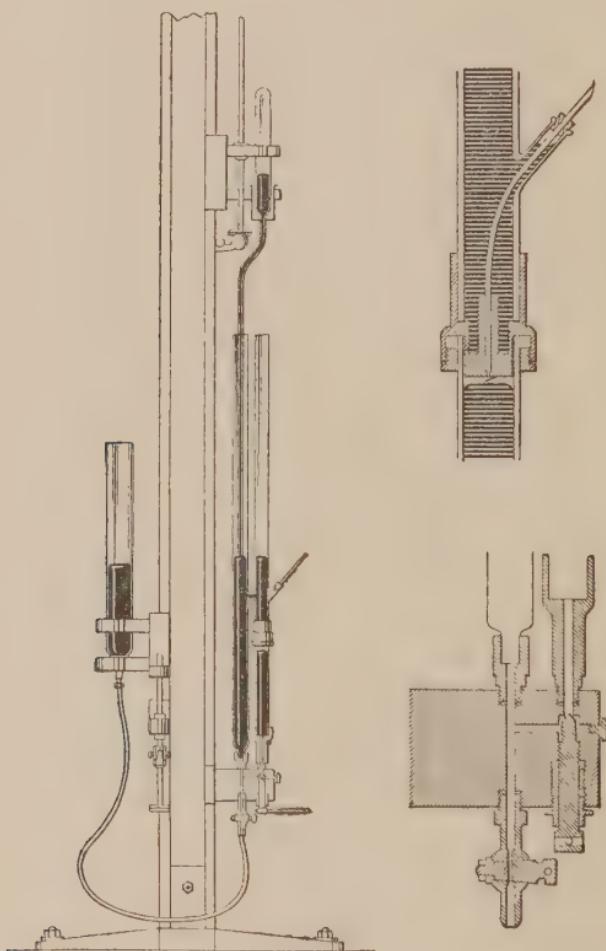


FIG. 2.

serves as axis in order to raise or lower the carriage with the barometer tube. This last has a diameter of 25 mm. in its upper part. The chamber is furnished with two indices of black glass soldered to the interior of the tube

at 0.08 m. and 0.16 m. from the end. The points of these indices, convex downwards, coincide sensibly with the axis of the barometric chamber. The part of the barometer which fits into the open manometer arm has a diameter greater than 0.01 m., and ends below in a narrower tube curved upwards.

The piece of steel which ends the closed arm is adjusted to this tube like a cock, leaving between itself and the tube but a very slight space, which is filled with sealing-wax. It rests upon the upper rim of this tube, to which it is besides pressed by leather washers tightly screwed up. At its lower end it terminates in a perfectly smooth polished plane, which is adjusted to be horizontal. In the middle of this surface, near to the opening of the canal which prolongs the joining tube, there is fixed a very fine platinum point, whose extremity, meant to be used as a reference-mark, is at a distance of about 0.6 mm. from the plane surface.

Above this piece is a tube of 25 mm. interior diameter, open above and connected below to the open arm of the manometer.

Since the measurement of a column of mercury is more easily made and with greater precision when the menisci whose difference of level it is desired to find are situated along the same vertical, the barometer is bent so as to bring into the same vertical line the axis of the closed arm of the manometer and that of the barometer. Under these conditions, the communication between the two manometer arms being established, the total pressure of the gas enclosed in the reservoir of the thermometer is given by the difference of level of the mercury in these superposed tubes.

The measurement of the pressures is made by means of a cathetometer furnished with three telescopes, each

of which is provided with a micrometer and level. The micrometer circle is divided into 100 parts; at the distance from which the manometer is read, each division of the circle corresponds to about 0.002 mm.

The method adopted for the measurement of pressures consists in determining the position of each mercury meniscus in terms of a fixed scale, hung near the manometer tubes, at the same distance as these latter from the telescopes of the cathetometer.

One of the principal difficulties arising in the measurement of pressures is that of the lighting of the menisci. The method employed by Chappuis consists in bringing up to the surface of the mercury an opaque point until its image reflected by the mercury appears in the observing telescope at a very small distance from that of the point itself. These two images being almost in contact, it is easy to set the micrometer cross-wire midway between them, at the precise point where would be the image of the reflecting surface. In order to have a very sharp image of the point, it is well to illuminate from behind by means of a beam of light passing through a vertical slit. The point and its image then stand out black on a bright background. The use of styles of black glass is preferable to that of steel points on account of their unchangeableness and of the greater sharpness of their edges.

The method with styles cannot be advantageously employed except in wide tubes, where the reflecting surface of the mercury which aids in the formation of the image does not have a sensible curvature.

Waste Space.—This consists of the space occupied by the gas: (1) in that part of the capillary tube which does not undergo the same variations of temperature as the thermometric reservoir; (2) in the piece of steel forming the plug which caps the closed arm of the manometer;

(3) in the manometer tube between the mercury and the horizontal plane in which ends the piece of steel. The mercury is supposed to just touch the style serving as reference-mark.

The capacity of the tube has been determined by mercury calibration; it was found equal to 0.567 cc. The length of the capillary tube being 1 m., if we deduct from this capacity that of 3 cm. of the tube which are exposed to the same temperatures as the reservoir, that is 0.015 cc., this leaves 0.552 cc.

The capillary tube fits for a length of 27 mm. into the piece of steel serving as plug. The total thickness of this plug is 28.3 mm.; thus the portion of the canal included between the end of the capillary tube and the lower face of the plug is 1.3 mm. in length. As its diameter is 1.35 mm., the capacity of this canal is 0.0019 cc.

The space included between a cross-section of the manometer tube passing through the style and the plane surface of the plug is 0.3126 cc.

To have the total volume occupied by the gas it is necessary to add as well to this space the volume of the depressed mercury in the manometric tube caused by the curvature of the meniscus. The radius of this tube being equal to 12.235 mm., we find for this volume 0.205 cc.

We thus have as the total of the waste space the sum of the following volumes:

	Cc.
Capacity of capillary tube.....	0.5520
Volume of canal in the plug.....	19
Capacity of the manometer tube between the style and the plane.....	3126
Volume of depressed mercury.....	2050
 Total waste space.....	 1.0715

When the mercury does not just touch the style, we shall have to add to this value, 0.4772 cc. per millimeter separation of the style from the top of the meniscus.

The *expansion of the metal of the bulb* has been measured by Fizeau's method; this volume has at different temperatures the following values:

	Liters.
20°.....	1.03846
0	1.03899
20	1.03926
40	1.04007
60	1.04061
80	1.04117
100	1.04173

The *variation of the capacity of the bulb* due to changes of pressure has also been studied; per millimeter of mercury it is 0.02337 $\overline{\text{mm.}}^3$; or

For 0 mm.....	$\overline{\text{mm.}}^3$
" 100	2.3
" 200	4.7
" 300	7.0
" 400	9.3

The zero is verified from time to time by bringing the bulb to the temperature of melting ice; there is absolute constancy even after heating to 100°. The deviation is at the most 0.03 mm. for a pressure of 995 mm.

Callendar's Thermometer.—For the graduation of the platinum resistance-thermometer Callendar has studied an arrangement of the gas-thermometer in which the waste space is reduced to a minimum by an ingenious device which consists in interposing in the capillary tube a column of sulphuric acid which is always brought to the

same position. It is then permissible to leave vacant spaces in the manometer of any volume, and this simplifies the measurements.

The *bulb* is of glass, and its capacity is 77.01 cc. The capillary tube has a diameter of 0.3 mm. It is attached to a small U tube of 2 mm. diameter which contains the sulphuric acid. The total value of the waste space is thus reduced to 0.84 cc.

The sulphuric acid before each measurement is brought up to a reference-mark. The density of this liquid being one-seventh that of mercury, the errors made in deter-

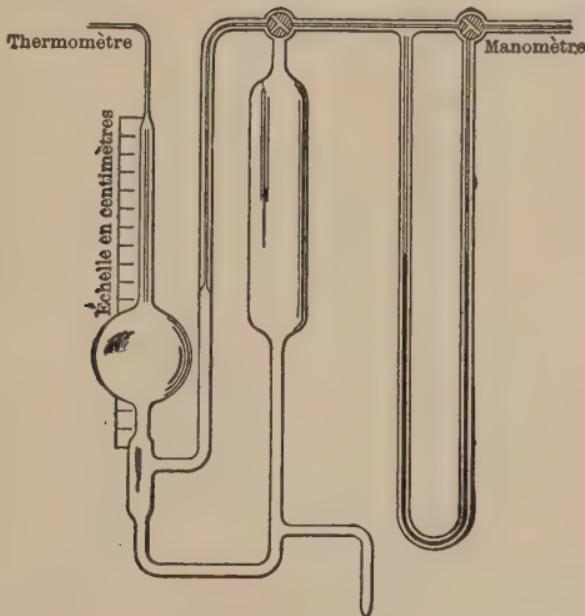


FIG. 3.

mining its level should be divided by seven to express them in heights of mercury. The use of this column of sulphuric acid has the inconvenience to oblige the experimenter to watch constantly the apparatus during the whole time of heating and cooling in order to maintain the pres-

sure equilibrium in the two parts of this column; otherwise the liquid would be driven into the manometer or absorbed into the bulb.

The *manometer* is one open to the air and is read conjointly with the height of the barometer.

The *coefficient of expansion* of the hard glass used in the construction of the thermometer was measured for a tube of same make by means of two microscopes carried upon a micrometer-screw. A cold comparison-tube could be placed under the microscopes to verify the invariability of their distance apart.

MEAN COEFFICIENT OF EXPANSION.

<i>t</i>	<i>α</i>
17°	0.00000685
102	706
222	740
330	769
481	810

After heating to 400° there were permanent changes amounting to from 0.02 to 0.05 per 100.

If the zero is taken at intervals of time of varying length, permanent displacements are noted. The following table gives some examples:

Date.	Oxygen-thermometer.	Nitrogen-thermometer.	Remarks.
	mm.	mm.	
Jan. 21, 1886	693.1	695.4	{ Filled at 300°; measurement taken 4 days later
" 22, "	692.9	695.1	
" 23, "	692.9	694.9	After heating to 100°
" 25, "	692.0	693.8	
" 25, "	692.0	694.1	" " " "

This change of zero has been attributed to a partial absorption of the air by the glass. Glass, an amorphous body resembling liquids somewhat, dissolves gases, especially at high temperatures.

For temperatures higher than 300° this source of error becomes very serious, especially if the gas is hydrogen. This gas disappears progressively by solution in the glass or by oxidation replacing elements of the glass. It is necessary to revert to nitrogen. This fact was observed by Chappuis and Harker in the course of a study of the platinum resistance-pyrometer when the temperatures measured reached as high as 600°.

One of the more recent forms of this thermometer in which there is complete compensation of the waste space is shown in Fig. 4, where *A* is the thermometer bulb connected by a capillary *a* to an overflow bulb, or, as here shown, to a burette *B*. The compensating capillary *b* is also connected to a bulb *C*, and across the two capillaries *a* and *b* is inserted the differential manometer *D*. The bulbs *C* and *B* for most exact work should be enclosed in a bath at constant temperature, as an ice bath. The relative sizes of the bulbs for the greatest accuracy will depend upon the temperature range to be studied. When equilibrium and compensation are established at any temperature the mass of the gas in the two parts of the apparatus will be the same if the pressures are adjusted to equality as shown by the sensitive manometer *D*, this supposing that *C* and *B* are at exactly the same temperature. For a change in temperature the volume change of the gas in *B*, *i.e.*, forced over from *A*, may be made by reading this volume on the burette or better by weighing the displaced mercury. The upper stop-cock serves to exhaust and fill the apparatus.

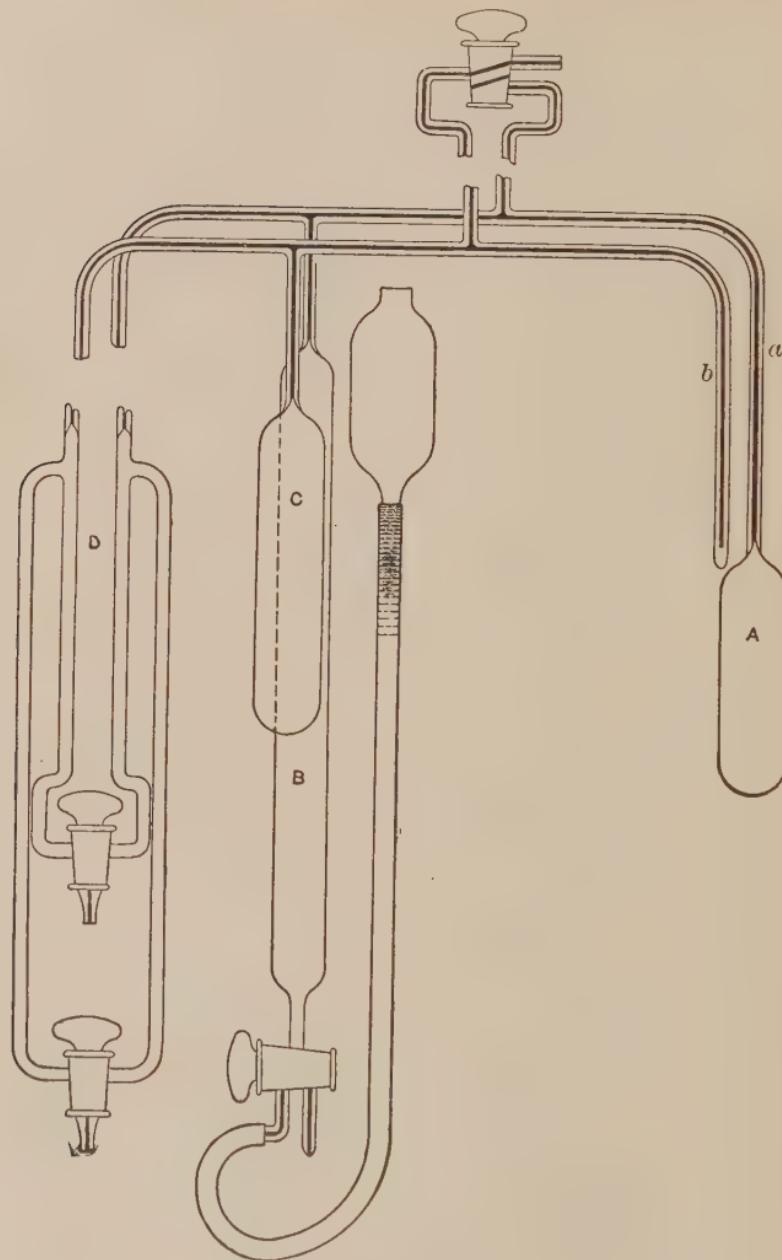


FIG. 4.

A determination of temperature is made as follows: for the compensating side of the apparatus we have

V_0 = volume of gas in C ;
 m_0 = mass " " " "
 θ_0 = temperature " " " " on gas scale;
 p_0 = pressure " " " "
 v = volume of capillaries;
 θ = average temperature of capillaries.

Then

$$p_0 \left(\frac{V_0}{\theta_0} + \frac{v}{\theta} \right) = mk,$$

where k is a constant.

For the thermometer proper we have, using a similar notation,

$$p_t \left(\frac{V_t}{\theta_t} + \frac{V_m}{\theta_m} + \frac{v}{\theta} \right) = m_1 k,$$

the subscript t referring to A , and $_m$ to B .

But $m_1 = m$ and $p_t = p_0$ as conditions of compensation; therefore

$$\frac{V_t}{\theta_t} + \frac{V_m}{\theta_m} = \frac{V_0}{\theta_0}.$$

But C and B are at the same temperatures, θ_0 , or $\theta_m = \theta_0$.

Finally

$$\theta_t = \frac{V_t \times \theta_0}{V_0 - V_m}.$$

Used with a quartz or platinum bulb such a gas-thermometer may become an instrument of the greatest accuracy for the experimental extension of the gas scale at constant pressure.

Thermometer for High Temperatures.—Up to the present time there has not yet been realized for the meas-

urement of high temperatures a gas-thermometer sufficiently precise to be considered a normal apparatus unless it be that of Holborn and Day, who have unquestionably carried the gas scale up to 1150° C. in a most satisfactory manner. We shall point out, in studying the gas-pyrometers, the conditions that such an apparatus should fulfil, and the reasons for these conditions. We shall in this place give only a brief summary.

The gas should be nitrogen or possibly helium.

The bulb should be of some platinum metal, as 80 Pt-20 Ir, or possibly quartz up to 1200° C.

The measurements should be made by the method of the thermo-volumenometer or by any other method which does not entail an invariability of the gaseous mass throughout a very considerable period of time.

In its actual condition the normal Sèvres thermometer permits of measurements up to 100°.

That of Callendar has been employed up to 600°, and could without doubt with a porcelain bulb be used up to 1000°, or even higher with quartz or platinum.

Holborn and Day have obtained most consistent results up to 1150° with a constant-volume nitrogen-thermometer in a 80 Pt-20 Ir bulb of 200 cc. capacity.

It would be possible to reach, by the method of the volumenometer, 1300°. To go higher it would be necessary to manufacture a special porcelain less fusible than the ordinary hard porcelain, or preferably use platinum or one of its alloys in an oxidizing atmosphere, by which means it might be possible to reach 1600°.

CHAPTER III.

GAS-PYROMETER.

THE gas-thermometer, as we have seen above, need not of necessity be used for the measurement of temperatures; it suffices to make use of it for the standardization of the different processes employed in the determination of temperatures, but *à priori* there are not on the other hand any absolute reasons for discarding it in cases other than these standardizations. Indeed it has often been employed. We shall examine some of the various trials that have been made with it, and discuss the results obtained.

Substance of the Bulb.—The most important point to consider is the choice of the substance which constitutes the bulb; it is necessary to know its expansion to account for the variation of its volume under the action of heat; one must be sure of its impermeability.

Five substances have been used up to the present time to make these bulbs: platinum, iron, porcelain, glass, and quartz.

Platinum, in spite of its high price, was employed by Pouillet and Becquerel; it has the advantage over iron in not being oxidizable, over porcelain in not being fragile. Its coefficient of expansion increases in a regular manner with temperature:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient.....	0.000007	0.000009

In the course of a noted controversy between H. Sainte-Claire-Deville and E. Becquerel the former of those savants discovered that platinum was very permeable to hydrogen, a gas whose presence is frequent in flames at points where the combustion is not complete. Platinum was accordingly completely abandoned, perhaps wrongly, it is possible, in very many cases, to be sure of the absence of hydrogen, and the very precise experiments of Randall have shown that red-hot platinum was quite impermeable to all gases other than hydrogen, even with a vacuum inside the apparatus.

Chappuis used a liter platinum-iridium bulb in his researches on the normal gas scale; and in the later investigations of Holborn and Day at the Reichanstalt in their comparison of thermocouple indications with the nitrogen scale up to 1150° C., bulbs of this material replaced porcelain to great advantage. As much iridium (15 to 20 per cent.) was contained in the alloy as permitted its shaping, giving an extremely rigid bulb and if the walls are 1.5 mm. thick, one which undergoes no appreciable deformation after being subjected to the considerable pressures required in the constant-volume gas-thermometer at high temperatures. This alloy is also impermeable to nitrogen, but must be guarded against reducing gases and silicates at high temperatures.

Holborn and Day also determined the coefficients of expansion of platinum, as well as other metals, alloys and porcelain.

For platinum and platinum-iridium they found:

$$\text{Platinum : } \lambda \cdot 10^9 = 8868t + 1.324t^2 \text{ from } 0^\circ \text{ to } 1000^\circ;$$

$$80 \text{ Pt} \cdot 20 \text{ Ir : } \lambda \cdot 10^9 = 8198t + 1.418t^2 \quad " \quad 0^\circ \quad " \quad 1000^\circ.$$

These determinations were made on bars nearly 50 cm. long in a most carefully constructed comparator heated

electrically. The uniformity of the expansion of platinum is shown by the fact that Benoît's determination by Fizeau's method in the interval 0°–80° C. gave

$$\lambda \cdot 10^9 = 8901 t + 1.21t^2.$$

So that in this case extrapolation of over 900° C. leads to no serious error.

Iron has but one advantage, its cheapness; it is as permeable to hydrogen as is platinum; it is not merely oxidizable in the air, but is besides attacked by carbonic acid and water-vapor. Thus the only gas that can be used with iron is pure nitrogen. The coefficient of expansion of iron is greater and increases more rapidly than that of platinum:

	Between 0° and 100°.	Between 0° and 1000°.
Mean linear coefficient.....	0.000012	0.000015

Also this increase is not regular; there is produced at 850°, at the instant of the allotropic transformation, a sudden change of length, a contraction of 0.25 per cent.

It is very difficult to obtain pure iron; very small quantities of carbon modify somewhat the value of the coefficient of expansion. Besides, the change of state of steel at 710°, corresponding to recalcination, is accompanied in the heating by a linear contraction, varying with the amount of carbon present, from 0.05 to 0.15 per cent.

Iron cannot therefore be seriously considered for work of any precision.

Porcelain was adopted as a result of the discussion between H. Sainte-Claire-Deville and Becquerel; it was considered as absolutely impermeable, but without decisive tests,

Even well-baked porcelain consists of a paste somewhat porous and permeable; it is only the glazing that assures its impermeability. But this covering may sometimes not be whole; as it softens above 1000°, it is susceptible of cracking if left for a considerable time with an excess of pressure on the interior of the apparatus. According to Holborn and Wien, the glazing is broken after reaching 1100°, when a considerable difference of pressure is established in the direction of the lifting up of this glazing.

Finally like all verres, porcelain dissolves gases, and in particular water-vapor, which passes through it quite readily. A pyrometer left a long time in the flame at about 1200°, becomes filled with water-vapor which can be seen to condense in the manometer after a few weeks.

The experiments of Crafts have shown that the rapidity of the passage of water-vapor through porcelain, in a pyrometer of from 60 to 70 cc. capacity at the temperature of 1350°, was 0.002 grm. of water-vapor per hour.

It is thus not safe to employ porcelain at temperatures higher than 1000°, at least not in the thermometric processes which suppose the invariability of the gaseous mass.

The expansion of porcelain has been the object of a great number of measurements which, for porcelains of very different make, give values near to one another; the mean linear coefficient between 0° and 1000° varies between 0.0000045 and 0.000005 for hard porcelain—that is to say, baked for a long time at a temperature in the neighborhood of 1400°.

Here are the results of experiments made by Le Chatelier and by Coupeaux; the experiments were made with porcelain rods 100 mm. in length, and the numbers express the elongation of these rods in millimeters:

Porcelain	Temperatures.					
	0°	200°	400°	600°	800°	1000°
Bayeux.	0.075	0.166	0.266	0.367	0.466	
Sèvres dure (cuite à 1400°).078	.170	.270	.378	.470	
Limoges.076	.168	.268	.360	.465	
Sèvres nouvelle (cuite à 1400°).090	.188	.290	.390	.490	

These numbers should be multiplied by three to give the cubical expansion.

Porcelain has still another inconvenience; the glazing is usually put on the outside only of vessels, so that the porosity of the paste gives an uncertainty due to the unequal absorption of gases at increasing temperatures.

According to Barus, it is impossible to fill with dry air a pyrometer, not glazed inside, at ordinary temperatures. The water is not driven out by pumping out several times and letting in dry air. An apparatus filled in this way will indicate between melting ice and boiling water from 150° to 200°. Nor is filling the apparatus at 100° satisfactory: it will indicate 115° for this same interval of 100°. Barus thinks that at 400°, by repeating the operation several times, one can consider the apparatus as filled with dry air.

The use of porcelain bulbs in several recent pyrometric researches of great importance has been the cause of outstanding differences in the determination of fixed points in pyrometry as the sulphur boiling-point, that are due mainly to the uncertainties in the expansion coefficient of the particular samples of porcelain used.

The work of Chappuis, Tutton, Bedford, and of Holborn, Day, and Grüneisen has shown the expansion of porcelain to be anomalous and that therefore extrapolation for

the coefficient cannot safely be made even over a hundred degrees for the most exact work. There is always a deformation of the bulbs of uncertain and irregular amounts in a constant-volume thermometer sufficient to render results doubtful at temperatures as low as 500° C., and Holborn and Day were unable with porcelain bulbs to get any considerable precision at 1000° C., and finally discarded them entirely.

They found for the expansion of Berlin porcelain

$$\lambda \cdot 10^9 = \{2954t + 1.125t^2\} \text{ from } 0^\circ \text{ to } 1000^\circ,$$

but this value is too high for temperatures below 250° as indicated by Chappuis, and Holborn and Grüneisen have shown that at about 700° C. a considerable change in the coefficient takes place, the expansion becoming more rapid at higher temperatures.

It would probably not be worth while to make further pyrometric studies with porcelain bulbs, when possible to avoid their use.

Glass cannot be used above 550° C., but in this range it may replace porcelain to advantage if Jéna Borosilicate 59^{III} is used, as the deformation after heating is somewhat less and more uniform. The coefficient of expansion of this glass as measured in the form of capillary tubes by Holborn and Grüneisen is

$$\lambda \cdot 10^9 = 5814t + 0.804t^2.$$

Quartz, in the amorphous or fused form, can now be made in vessels of several hundred cubic centimeters capacity, thanks to many attempts culminating successfully in the efforts of Heraeus, and Siebert and Kühn. The chemical and physical properties in view of its pyrometric use have been studied by many investigators,

Shenstone being a pioneer in advocating its use in thermometer bulbs. Vitrified quartz vessels seem to resist deformation at very high temperatures, the upper limit when the interior is a vacuum being not far from 1300° C.; the substance is appreciably plastic at 1500°, but a quartz vessel will not collapse until 2000° is reached, according to Heraeus.

Fused quartz is attacked by alkalies, and the slightest trace of such, as from handling, may do damage when the heating is carried very high. Weak acids and neutral salts are without effect as shown by Mylius, but at high temperatures all oxides attack it. Heated with a porcelain tube to very high temperatures the quartz tends to lose its transparency, and Moissan has shown that it is slightly soluble in a lead bath above 1100° C., and very much more so in zinc. Villard showed that it is permeable to hydrogen but less so than platinum, nor does it seem to occlude other gases; it is less brittle than porcelain.

Its great advantage in gas thermometry is its lack of deformation and its extremely small coefficient of expansion, about $\frac{1}{17}$ that of platinum, or, more exactly, as determined by Holborn and Henning with a comparator;

$$\lambda \cdot 10^9 = 540t \text{ from } 0^\circ \text{ to } 1000^\circ.$$

Scheel, using a Fizeau apparatus, finds

$$\lambda \cdot 10^9 = 322t + 1.47t^2 \text{ between } 0^\circ \text{ and } 100^\circ,$$

where the curvature is of the same order as for metals.

In work at 1000° C. the expansion correction is reduced from over 20° with porcelain or platinum to about 1°, and its uncertainties become therefore negligible, permitting a great increase in accuracy. Several investigations

are now under way using quartz bulbs, and a final judgment as to its availability will have to await the completion of this work.

Corrections and Causes of Error.—1. *Thermometer at Constant Volume.*—We must now render more precise the formula of the air-thermometer, by taking account of the variations of volume of the bulb, of the surrounding air-temperature which changes the density of the mercury, and finally of the volume of the waste space.

We have three series of observations to make in order to determine a given temperature:

$$P_0 V_0 = n_0 R T_0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

$$P_{100} V_{100} = n_{100} R T_{100}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

$$P V = n R T. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

Putting

$$T = \frac{1}{\alpha} + t;$$

the first two series serve to determine $\frac{1}{\alpha}$.

It is preferable, except in researches of very great precision, to take $\frac{1}{\alpha}$ from previously obtained results, and not to make the observations at 100° , unless one does so to check his experimental skill.

Dividing the third equation by the first, we have the relation

$$\frac{P V}{P_0 V_0} = \frac{H \Delta_0 V}{H_0 \Delta V_0} = \frac{n R T}{n_0 R T_0} = \frac{n T}{n_0 T_0}, \quad \dots \quad \dots \quad \dots \quad (4)$$

where H and H_0 are the heights of mercury, Δ and Δ_0 the densities of this metal.

For a first approximation let us neglect the differences

between V and V_0 , n and n_0 , A and A_0 . We shall have then an approximate value T' for the temperature sought:

$$T' = \frac{1}{\alpha} \cdot \frac{H}{H_0}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

for

$$T_0 = \frac{1}{\alpha}.$$

Let us find now the *correction* dT to T' to obtain the exact temperature. In order to find this, take the logarithmic differential of (4):

$$\frac{dT}{T'} = \frac{dA}{A_0} + \frac{dV}{V_0} - \frac{dn}{n_0}. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (6)$$

Then determine the values of the different terms; let t_1 and t_2 be the absolute temperatures of the surroundings when the bulb is at the temperatures T' and T_0 .

$$1. \quad \frac{dA}{A_0} = \frac{A - A_0}{A_0},$$

$$A = A_0 \cdot [1 - k(t_2 - t_1)],$$

$$k = 0.00018(t_2 - t_1),$$

$$\frac{dA}{A_0} = -0.00018(t_2 - t_1)$$

$$2. \quad \frac{dV}{V_0} = \frac{V - V_0}{V_0},$$

$$V = V_0[1 + k'(T' - T_0)],$$

$$k'(\text{porcelain}) = 0.0000135.,$$

$$\frac{dV}{V_0} = 0.0000135(T' - T_0),$$

by neglecting the variations of volume of the bulb due to changes of pressure,

$$3. \quad -\frac{dn}{n_0} = \frac{x_2 - x_1}{n_0},$$

in calling x_2 and x_1 the number of molecules contained in the waste space ϵ at the temperatures t_2 and t_1 . We have in fact, N being the total mass contained in the apparatus,

$$\begin{aligned} n &= N - x_2, \\ n_0 &= N - x_1, \\ n - n_0 &= -(x_2 - x_1). \end{aligned}$$

To determine x_1 and x_2 :

$$\begin{aligned} P_0 \epsilon &= x_1 R t_1, \\ P \epsilon &= x_2 R t_2, \end{aligned}$$

$$-\frac{dn}{n_0} = \frac{\epsilon}{V_0} \left(\frac{P}{t_2} - \frac{P_0}{t_1} \right) \cdot \frac{T_0}{P_0}.$$

In noting that

$$\frac{P}{P_0} = \frac{T'}{T_0},$$

we have

$$-\frac{dn}{n_0} = \frac{\epsilon}{V_0} \left(\frac{T'}{t_2} - \frac{T_0}{t_1} \right).$$

Put

$$t = \frac{t_1 + t_2}{2},$$

$$\theta = \frac{t_2 - t_1}{2}.$$

After substitution we have

$$\frac{dn}{n_0} = -\frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' + T_0}{t} \right).$$

These successive transformations are for the purpose of making evident from the formula:

1. The ratio between the waste space and the total volume: $\frac{\epsilon}{V_0}$;
2. The temperature measured: $T' - T_0$;
3. The variation of the surrounding temperature θ ;

which are the three essential factors on which depends the correction in question.

Formula (6) then becomes:

$$\frac{dT}{T'} = -0.00018(t_2 - t_1) + 0.0000135(T' - T_0) - \frac{\epsilon}{V_0} \cdot \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' - T_0}{t} \right).$$

Let us take a numerical example in order to show the importance of these correction terms in the three following cases:

$$T' - T_0 = 500^\circ,$$

$$T' - T_0 = 1000^\circ,$$

$$T' - T_0 = 1500^\circ.$$

In taking

$$\frac{\epsilon}{V_0} = 0.01,$$

$$t = 27^\circ + 273^\circ = 300^\circ,$$

$$2\theta = 10^\circ,$$

we have

$$dT_{500} = -1^\circ.4 + 5^\circ.15 + 13^\circ.1 = 16^\circ.85,$$

$$dT_{1000} = -2^\circ.3 + 17^\circ.0 + 38^\circ.2 = 52^\circ.9,$$

$$dT_{1500} = -30^\circ.7 + 35^\circ.7 + 90^\circ.0 = 122^\circ.5.$$

These figures show the very great importance of the waste space, whose exact volume it is impossible to know. T! is

method of computation of the corrections by logarithmic differentials is only approximate, and is not sufficient for real measurements, but it renders more clear the general discussion of the causes of error.

Let us see what uncertainty in the temperature may result from the uncertainty which there may be in the volume of the waste space. In reality there is a continuous passage from the high temperature of the pyrometer to the surrounding temperature on a length which may vary from 10 to 30 centimeters, according to the thickness of the walls of the furnace. The volumes of the bulb and of the waste space which should be taken in order that the above formulas be exact should be such that the real pressure is equal to the pressure that would exist in supposing that a complete and sudden change of temperature took place at a definite fictitious point, separating the heated part from the cold part of the apparatus. The probable position of this point is estimated, and, if the estimation is poorly made, two errors are committed, one on the real volume heated and the other on the waste space, errors equal and of opposite sign so far as the volume is concerned.

To calculate this *error*, as in the case of the corrections, we may employ the method of logarithmic differentials.

Applying the same formula as before, we find for the relative error $\frac{dT}{T}$:

$$\frac{dT}{T} = -\frac{dV}{V_0} \left(\frac{T' - T_0}{t} - \frac{\theta}{t} \cdot \frac{T' + T_0}{t} \right);$$

and neglecting the second term of the parenthesis, which is relatively very small,

$$\frac{dT}{T} = -\frac{dV}{V_0} \left(\frac{T' - T_0}{t} \right).$$

Letting the section of the capillary tube be equal to 1 sq. mm., the volume of the bulb 100 cc., and assuming an uncertainty of 100 mm. in the position of the transition-point, a value often not exaggerated, we find the following errors in the temperatures:

$$\begin{aligned}dT_{500} &= 1^{\circ}.7, \\dT_{1000} &= 3^{\circ}.9, \\dT_{1500} &= 8^{\circ}.5.\end{aligned}$$

We thus see that at 1000° the error resulting from the uncertainty in the origin of the waste space may reach several degrees for a bulb of 100 cc.

A second cause of error results from the changes of mass following the ings and outgoings of gas. As before, we have

$$\frac{dT}{T} = -\frac{dn}{n_0}.$$

Consider the experiments of Crafts. There enters per hour at 1350° in a bulb of porcelain of 100 c.c., 0.002 grm. of water-vapor, or 0.225 milligramme-molecules; the initial volume enclosed at the start is 4.5 milligramme-molecules:

$$\frac{dT}{T} = \frac{0.225}{4.5} = 0.05,$$

which leads to an error of

$$dT_{1350^{\circ}} = 70^{\circ} \text{ (about)}$$

for an experiment lasting one hour.

This computation demonstrates clearly the enormous errors which may result from the penetration of an outside

gas during the time of one hour, a length of time much less than that of an ordinary experiment. It is true that this error decreases rapidly with rise of temperature, and it is very probably zero at 1000°, if there is no break in the glazing.

2. *Constant-pressure Thermometer*.—We still employ the same formula (4):

$$\frac{H\Delta V}{H_0\Delta_0 V_0} = \frac{nRT}{n_0 R_0 T_0},$$

which gives for a first approximation

$$\frac{T'}{T_0} = \frac{n_0}{n}.$$

Calling t_1 and t_2 the surrounding absolute temperatures corresponding to T_0 and T_1 , u_1 and u_2 the corresponding volumes of the waste space and of the reservoir, we have, for the determination of n and n_0 , the relations:

$$n_0 = N - x_1 = \frac{H_0 \Delta_0 V_0}{t_2 \cdot t_1},$$

$$n = N - x_2 = n_0 - (x_2 - x_1),$$

$$x_2 = \frac{H \Delta u_2}{R t_2},$$

$$x_1 = \frac{H_0 \Delta_0 u_1}{R t_1}.$$

As before, there is a correction to be applied to the approximate temperature T' thus obtained:

$$\frac{dT}{T'} = \frac{dH}{H_0} + \frac{d\Delta}{\Delta_0} + \frac{dV}{V_0},$$

an expression the values of whose terms are known.

Let us see now the causes of error and discuss their importance.

The error resulting from the uncertainty in the boundary of the hot and cold volumes is

$$\frac{dT}{T'} = \frac{dn_0}{n_0} - \frac{dn}{n} = \frac{dn}{n_0} \left(1 - \frac{T'}{T_0}\right) = -\frac{dn_0}{n_0} \left(\frac{T' - T_0}{T_0}\right).$$

As before let,

$$\frac{dn}{n_0} = \frac{1}{1000}.$$

Then we find

$$dT_{500} = 1^\circ.5,$$

$$dT_{1000} = 5^\circ.0,$$

$$dT_{1500} = 9^\circ.3.$$

Thus the errors due to this cause are still greater than by the method of constant volume.

In order to make exactly the correction for the waste space, the method of Regnault's compensator may be employed, as in the work of Sainte-Claire-Deville and Troost; this allows of placing the measuring apparatus at a considerable distance from the fire, which makes the experiments much easier.

Let us now examine the error resulting from the entrance of exterior gases:

$$\frac{dT}{T'} = \frac{dn}{n} = \frac{dn_0}{n_0} \cdot \frac{T}{T_0}.$$

For the experiment of Crafts, the error would be 413° instead of 70° , the bulb being filled at the start at atmospheric pressure.

It is thus evident that, from all points of view, the method of constant volume is more precise than that of

constant pressure; the lack of impermeability of the coverings is the only hindrance preventing the use of the former in practice.

3. *Volumenometric Thermometer.* — The only rational method for the measurement of high temperatures is, as we have already said, that of the volumenometer of Becquerel, which does not require the invariability of the gaseous mass throughout the duration of the experiment. It consists in measuring the changes of pressure resulting from a given variation of the gaseous mass contained in the bulb. Becquerel employed very slight changes of mass; the changes of pressure are then equally slight, which diminishes the precision of the measurements.

There is no theoretical inconvenience in reaching an absolute vacuum, or, what is practically more simple, using the exhaustion given by a water-pump, as was done by Mallard and Le Chatelier; this considerably increases the precision. If the exhaustion is complete, we have the relation

$$\frac{PV}{RT'} = n = \frac{P_0 u_0}{RT_0},$$

u_0 being the volume of the reservoir corresponding to the surrounding temperature T_0 . If the two volumes are filled under atmospheric pressure, $P = P_0$, and then

$$\frac{T'}{T_0} = \frac{u}{V}.$$

There are two corrections to make: the first relative to the expansion of the envelope, the second to the difference between P and P_0 when the exhaustion is produced by a water-pump:

$$\frac{dT}{T'} = \frac{dP}{P} + \frac{dV}{V}.$$

In general dP is in the neighborhood of 15 mm. of mercury, which gives

$$\frac{dP}{P} = 0.02.$$

Also,

$$\frac{dV}{V} = 0.0000135(T' - T_0),$$

$$\frac{dT}{T'} = -0.02 + 0.0000135(T' - T_0).$$

Calculating this correction for different temperatures, we have

$$dT_{500} = -10^{\circ}.4,$$

$$dT_{1000} = -8.5,$$

$$dT_{1500} = -0.35.$$

Let us compute now the error which comes from the uncertainty in the position of the line of separation of the warm part and the cold part of the apparatus; it is, besides, the only remaining one:

$$\frac{dT}{T'} = \frac{dV}{V}.$$

As before, assuming the higher limit to be $\frac{1}{1000}$,

$$\frac{dT}{T'} = \frac{1}{1000},$$

which leads to

$$dT_{500} = 0^{\circ}.77,$$

$$dT_{1000} = 1.27,$$

$$dT_{1500} = 2.77.$$

From every point of view, this method is thus preferable to the others.

This whole discussion of the sources of error in the measurement of temperatures aims merely to obtain a determination of the temperature of the pyrometer employed. But this temperature is in itself not the real object of the measurements; it is but an intermediary to arrive at a knowledge of the temperature of certain other bodies supposed to be in thermal equilibrium with the pyrometer. Now this equilibrium is extremely difficult to realize, and it is more often the case that there is no way of being sure of the exactitude with which it has been obtained. Here is then a new source of error very important in the measurement of temperatures, especially of high temperatures, at which radiation becomes an important consideration. Within an enclosure whose temperature is not uniform, which is true for the majority of furnaces, there may exist enormous differences of temperatures between neighboring parts. One cannot too strongly insist upon the presence of this source of error, with whose existence too many investigators have not sufficiently occupied themselves.

Experimental Results.—We shall study now the experiments made by various savants, and we shall see in what degree the conditions of precision indicated in the course of this account have been realized.

Experiments of Pouillet.—Pouillet was the first to make use of the air-thermometer for the measurement of high temperatures; he obtained very good values for the epoch at which he worked.

His pyrometer was made of a platinum bulb, of ovoid form, of 60 cc. capacity, to which was gold-soldered a platinum capillary tube of 25 cm. in length; continuous with this tube was another of silver of the same length

fastened to the manometer. The joining of the platinum and silver tubes was made by means of a metal collar (Fig. 5). The waste space had thus a volume of 2 cc.



FIG. 5.

The manometer was made up of three glass tubes embedded at their lower ends in a metallic piece: the first tube serving as a measurer was graduated in cubic centimeters, the second constituted the manometer properly speaking, and the third served to fill the apparatus.

A cock conveniently placed permitted variation of the quantity of mercury contained in the apparatus (Fig. 6). The principle of this apparatus is the same as that of the more recent Regnault manometer; this latter differs from the manometer of Pouillet only in the suppression of the third tube, which is replaced by a bottle joined to the emptying-cock by a rubber tube.

Errors: 1. According to Pouillet, it was impossible to carry the measurements up to 1200° ; there was complete disaccordance with the readings of the mercury-thermometer. He attributed this non-agreement to the condensa-

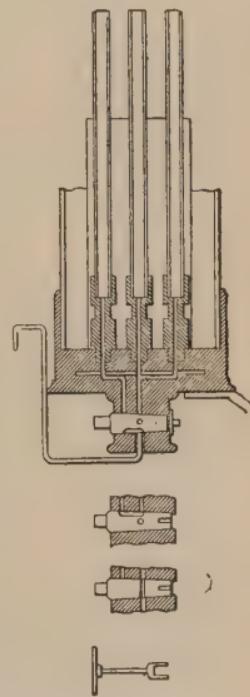


FIG. 6.

tion of air on the platinum. Becquerel showed later that this was due to the presence of water-vapor in the insufficiently dried air.

2. Not being able to use the 100° mark for the determination of the coefficient of expansion of air, Pouillet took the number 0.00375, given by Gay-Lussac, instead of the correct number, 0.00367. This is the principal source of error in his measurements. The following table permits a comparison of his results for the specific heats of platinum with those obtained by Violle:

	100°	300°	500°	700°	1000°	1200°
Pouillet, $\alpha = 0.00375$. . .	0.0335	0.0343	0.0352	0.0360	0.0373	0.0380
“ $\alpha = 0.00367$. . .	32	336	345	353	366	373
Violle.	323	535	347	359	377	389

Fusing-points.—Pouillet's determinations of fusing-points are far less good:

Gold.	1180° (too high by 115°)
Silver.	1000 (“ “ “ 40°)
Antimony.	432 (too low by 200°)
Zinc.	423 (good)

The possible sources of error are the following:

1. Introduction of hydrogen into the platinum bulb, which should raise too high the temperature-measurement and diminish the specific heat of platinum; the fusing-points of gold and silver are too high.

2. Equilibrium of doubtful temperature with the furnace as arranged. A glass tube, heated from below by coal, would necessarily be more strongly heated near the base; it would then have been necessary, in order to have accurate measurements by this arrangement, certainly

very irregular as to temperature, that the substance and the thermometer be in the same conditions with respect to radiation (Fig. 7).

For antimony the error is certainly due to some particular cause; or perhaps the very impure metal was mixed with lead, or there may have been a mistake in computation. Nevertheless the number 432 was the only one used up to the recent memoir of Gautier on the fusibility of alloys.

Experiments of Ed. Becquerel.

—This savant took up and continued the work of Pouillet with the same apparatus. But at the close of a discussion with H. Sainte-Claire-Deville on the question of the permeability of platinum, he made use successively of pyrometers of iron and of porcelain. The results obtained with platinum seem, however, to be far the best.

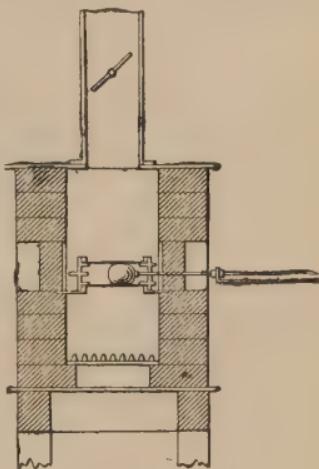


FIG. 7.

	Pyr. of Pt.	Pyr. of Porcelain.
Boiling-point of zinc.	930° (good)	890°
Fusing-point of silver.	960 "	916
Fusing-point of gold.	1092	1037

The figures for gold differ among themselves by about 25°, more or less.

It is difficult to explain these differences, which are probably due to inequality of temperature between the pyrometer and the metal under investigation, resulting perhaps from a difference in their emissive powers.

Experiments of H. Sainte-Claire-Deville and Troost.—They, after their discussion with Becquerel, made numer-

ous experiments with the porcelain air-thermometer; they obtained very discordant results, which they did not publish at the time.

They placed the most confidence in the determinations made by the aid of the vapor of iodine (we shall speak of this later); but when the inaccuracy of this method was pointed out, they made known the results that they had obtained for the boiling-point of zinc.

They employed a crucible of plumbago having a capacity of 15 grms. of zinc; the metal was added anew as fast as it evaporated.

The crucible was placed in a furnace filled with coal. Around the pyrometer was arranged a covering of fire-clay; but this arrangement was quite insufficient to eliminate errors due to radiation. The same measurements were repeated with different gases.

Figures obtained:

Gas.		First Series.	Second Series.	Third Series.
Air.....	From	945° to 955°	940° to 948°	928° to 932°
Hydrogen.....	"	925 to 924	916 to 924	
Carbonic acid.....		1067	1079	

The deviations seem to be a function of the nature of the gas, which is inexplicable; it would be necessary to admit of an enormous dissociation of the carbonic acid in order to explain the temperatures found with this gas.

Later this method was modified. The gas enclosed in the pyrometer was removed by means of the mercury-pump, either warm or after cooling. But this method did not possess any real advantages; the entrance of the gas and vapors during the reheating is not avoided; besides, during the cooling, there is danger of the entrance of air by leak-

ing of the cock placed at the outlet of the pyrometer. Troost found in this way 665° for the boiling-point of selenium; this figure is too high. As in the case of the determination of the boiling-point of zinc, the arrangement for heating did not protect sufficiently against the radiation from the outer surfaces.

Violle's Experiments.—Guided by H. Sainte-Claire-Deville, whom his successive failures had instructed in the difficulties of the problem, Violle has made a series of measurements which are among the best up to the present time. He made use of a porcelain thermometer, and he worked simultaneously at constant pressure and constant volume. The agreement of the two numbers shows if the mass has remained constant; this is the equivalent of the method of Becquerel.

The most serious objection that can be made to these observations is as to the uncertainty of the equality of temperatures of the pyrometer and of the substance studied placed beside the former; from this point of view, however, these experiments, made in the Perrot furnace, were much more satisfactory than those made in coal-furnaces previously employed.

1. A first series of determinations was of the specific heat of platinum. A platinum mass of 423 grm. was put into a Perrot muffle alongside the pyrometer, and when the mass was in a state of temperature-equilibrium it was immersed, either directly in water or in a platinum eprouvette placed, opening upward, in the midst of the calorimeter-water. In the first case the experiment was made in a few seconds; in the second it lasted fifteen minutes, and the correction was as high as $0^{\circ}.3$ per 10° ; the results, however, were concordant. At 787° two experiments gave 0.0364 and 0.0366; mean, 0.0365.

At 1000° twelve experiments were made employing the

method of immersion; the numbers found vary from 0.0375 to 0.0379; mean, 0.0377.

Near 1200° the measurements were made at constant pressure and at constant volume.

Temperature at Constant Volume:	Temperature at Constant Pressure.	Mean.	Specific Heat of Platinum.
1171°	1165°	1168°	0.0388
1169	1166	1168	.0388
1195	1192	1193	.0389

The mean specific heat may be represented by the formula

$$C_0 t = 0.0317 + 0.000006 \cdot t.$$

The true specific heat is equal to

$$\frac{dq}{dt} = 0.0317 + 0.000012 \cdot t.$$

Violle used these determinations to fix, by extrapolation, the fusing-point of platinum, which he found equal to 1779°. He measured for that the quantity of heat given out by 1 grm. of solid platinum from its fusing-point to 0°. For this purpose a certain quantity of platinum is melted, into which is plunged a spiral wire of the same metal, and, at the instant that the surface of the bath solidifies, by aid of this wire a cake of solid platinum is lifted out and immersed in the water-calorimeter. Repeating the determination of this fusing-point, Holborn and Wien have found more recently 1780°.

The latent heat of fusion of platinum is equal to

74.73 c.±1.5; this number results from five determinations.

2. A second series of experiments was on the specific heat of *palladium*; the determinations were made, in part by comparison with platinum, in part by the air-thermometer. The results obtained by the two methods are concordant.

The mean specific heat is given by the formula

$$C_0^t = 0.0582 + 0.000010 \cdot t.$$

The true specific heat is equal to

$$\frac{dq}{dt} = 0.0582 + 0.000020 \cdot t.$$

The fusing-point was found equal to 1500°; the more recent experiments of Holborn and Wien give 1580°. This difference can be explained by impurities in the metal and absorption of furnace-gases.

The latent heat of fusion of palladium, measured by the same experiments, was found to be 36.3 calories.

3. In another series of experiments Vioille has determined the boiling-point of zinc. He employed an apparatus of enamelled casting, heated in a triple envelope of metallic vapor; the top was covered with clay and cow-hair to prevent superheating of the coverings. The measurements were made with pressure and volume simultaneously variable.

Volume of bulb.....	294.5 cc.	Volume of gas let out	184.3 cc.
Waste space.....	4.7 "	Pressure	892.3 mm. $T = 929^{\circ}.6$
t_0	3°.8	t_0	7°.7
H_0	760.5 mm.	H_0	759.5 mm.

Barus, Holborn and Wien found numbers very close to 930°.

4. A last series is relative to the fusing-points of metals, which were determined by comparison with the total heat of platinum:

Silver.....	954° (too small by 10°)
Gold.....	1045 (" " " 20)
Copper.....	1050 (" " " 15)

Experiments of Mallard and Le Chatelier.—In their investigations on the temperatures of ignition of gaseous mixtures, Mallard and Le Chatelier made use of a porcelain pyrometer, which was exhausted, then air was let in and the gaseous volume thus absorbed was measured. It is possible to reach 1200° without noticing any breaking down of the porcelain; but this giving way is complete at 1300° under the action of the vacuum.

This method was used in the following way to measure the temperatures of ignition of gaseous mixtures. The air was exhausted from the apparatus, and the temperature was measured by the air-volume which filled it; the air was again exhausted and the apparatus was filled with the gaseous mixture. Whether or not there was ignition was known by the comparison of the volume of the mixture with that of the air introduced under the same conditions of temperature, at least in the cases of mixtures burning with contraction.

The pyrometer used had a capacity of 62 cc., after deduction of the waste space (1 cc.); the following table gives the volumes of air corresponding to different temperatures:

400°.....	26.7 cc.
600	20.6
800	16.7
1000	14.1
1200	12.2

In admitting that the measurements of volume be made to 0.1 cc., one should have a precision of only 10° in 1000° on account of the insufficient volume of the thermometric reservoir.

Experiments of Barus.—This American savant devised a rotating apparatus, remarkable for its uniformity of temperature, but he applied it directly only to the standardization of thermoelectric couples. He worked at constant pressure. By means of couples graduated in this way, he has determined the boiling-points of zinc (926° – 931°) and of cadmium (773° – 784°); the boiling-point of bismuth was found equal to 1200° under a reduced pressure of 150 mm., which would give under atmospheric pressure by extrapolation 1500° .

Fig. 8 represents the longitudinal section of Barus' apparatus. It is composed essentially of a porcelain

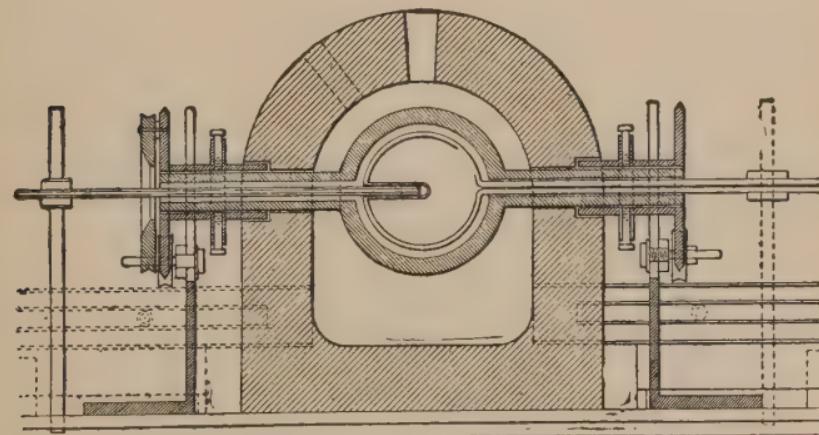


FIG. 8.

pyrometer containing an interior tube in which is placed the couple. The pyrometer fixed at a point of its stem is held stationary. It is surrounded by a muffle of casting whose general shape is that of revolution about the axis

of the pyrometer; this muffle is composed of two similar halves held by means of iron collars, and can be given a motion of rotation about its axis of figure, in such a manner as to assure uniformity of heating. It is heated by gas-burners placed below. An outer covering of fire-clay keeps in the heat about the iron muffle.

Experiments of Holborn and Wien.—Holborn and Wien have made a very complete standardization of the thermo-electric couple Pt—Pt—Rh proposed by Le Chatelier. They made use of a porcelain reservoir of about 100 cc. capacity, terminating at its two ends in capillary porcelain tubes. The thermoelectric junction is placed inside the bulb, and each of its wires is led out by one of the lateral tubes; this arrangement allows of determining at various points the real temperature of the waste space whose volume is 1.5 cc.

They worked at constant volume, with a very low initial pressure so as always to have depression; they were able to reach 1430°. Above 1200° they could make but a single observation with one pyrometer; below this, about ten observations.

They determined the coefficient of expansion of their porcelain, a product of the Berlin works, and found it equal to 0.0000045, the identical number given by Le Chatelier for the Bayeux porcelain.

They made use of this pyrometer, employing as intermediary a couple, to fix the fusing-points of certain metals:

Silver.....	970°
Gold.....	1072
Palladium.....	1580
Platinum.....	1780

These figures, at the time they were obtained, were counted among those which seemed to merit the most

confidence; however, it is necessary to note that the volume of the bulb was too small to assure a very great accuracy.

We shall return to these experiments when treating of electric pyrometers.

Holborn and Day's Investigations.—The work of establishing the gas-scale upon a satisfactory basis was continued at the Reichsanstalt by Holborn and Day, who also determined the thermo-couple scales in terms of that of the nitrogen constant-volume thermometer as well as establishing several fixed points.

Their preliminary work was done with porcelain bulbs at temperatures above 500° C. using nitrogen and hydrogen and with a bulb of Jéna borosilicate glass No. 56^{III} filled with hydrogen for temperatures below 500°. Porcelain bulbs glazed outside and also unglazed bulbs were used. Errors due to changes in the bulbs were detected by taking "zero" readings and also by the simultaneous use of thermocouples. Salt baths were used up to 900° at first, but later electric heating was employed in all the high temperature work.

The hard glass bulbs of about 167 cm. capacity showed less changes, after annealing, than the irregularities in the thermocouple measurements, due to the lack of sensitiveness of the latter at low temperatures; and these glass bulbs were found preferable to those of porcelain up to 500° C. The precision attainable with thermo-couple control was about 0°.6 C.

Porcelain bulbs of 100 cc. capacity glazed inside and out, filled with hydrogen and heated to only 700°, gave very discordant results due apparently to chemical action between the hydrogen and the walls of the bulb and to water-vapor generated. Used with nitrogen and heated electrically to about 1100° C. the mean difference between

the observed and calculated values was $\pm 1^{\circ}.5$ C. Far less satisfactory results were obtained with porcelain glazed only on the outside.

A first series of experiments with a metal bulb were made with a 20 per cent iridium alloy of platinum, the bulbs being cylindrical of 208 cc. volume and 0.5 mm. wall and the waste space was considerably reduced over that of the porcelain bulbs. The electric heating oven was also improved by winding it logarithmically so that at 1150° the temperature distribution was constant to 3° over that portion of the oven containing the bulb. This was still further equalized by the presence of the metallic bulb; also at very high temperatures the tendency to equilibrium through radiation balances more nearly the losses by end conduction. Temperature control to $0^{\circ}.1$ C. at 1000° C. may be realized electrically with care. A precision of better than 1° C. was then obtained, and the conclusion seemed warranted that the metallic bulbs in an electrically-heated furnace, where no gases or other materials acting upon platinum were in contact with it, were superior to any form of porcelain bulb.

Their later work consisted in a determination of fixed points using the thermocouple as intermediary, after having found the coefficient of expansion of the material of their bulb and shown that the bulb underwent no deformation after heating. The correction for expansion amounts to 30° at 1000° and 40° at 1150° . The expansion was determined for a 50 cm. bar in a comparator which could be heated electrically to 1000° C.

Although no change in volume of the thin-walled bulb could be detected on cooling, a temporary yielding of the glowing walls under the comparatively high pressure might have taken place, so a bulb having walls 1 mm. thick was substituted, the composition being 90 Pt-10 Ir. This bulb was as satisfactory as the first.

The results obtained by Holborn and Day for the fixed points, as well as their work with thermo-elements, will be discussed later.

Experiments of Jacquierod and Perrot.—Only a preliminary publication of this work has as yet been made. Using a quartz bulb filled at constant volume successively with nitrogen, air, oxygen, carbon monoxide, and carbonic acid, and employing an electric resistance furnace, results agreeing to $0^{\circ}.3$ were obtained for the fusing-point of gold with the first four gases using a common coefficient of expansion based on Chappuis limiting value and using varying initial pressures. The use of quartz reduces the correction for the expansion of the bulb to 2° at 1000° .

This work shows that in the range 0 – 1100° C. the coefficients of expansion of these gases are practically identical.

Arrangement of Experiments.—The discussion that we have just held permits us to define certain conditions to which should conform new experiments necessary to further the accuracy of fusing and boiling temperatures used as fixed points for the standardization of other pyrometers.

Before Holborn and Day had demonstrated the superiority of an iridium alloy of platinum for the bulb, it seemed preferable to recommend that the bulb of the thermometer be of porcelain enamelled inside and out, as were the bulbs made at Sèvres for certain experiments of Regnault and of H. Sainte-Claire-Deville. Quartz may be found preferable up to 1200° C.

The capacity of the bulb should be as nearly as may be as great as 500 cc., the condition necessary in order that the error resulting from the waste space be certainly less than 1° .

It may be desirable to immerse the manometer and other exposed parts in a water-bath to insure a constant temperature.

The thermometric gas will be nitrogen, or perhaps helium.

The volumenometer method should be employed, or any equivalent method which does not suppose the invariability of the gaseous mass, and the greatest changes of pressure compatible with the resistance of the material will be produced. Up to 1200° a high vacuum should be employed, since there is no danger of deforming the bulb.

Finally, most careful precautions will be taken to assure the equilibrium of temperature between the reservoir of the pyrometer and the body whose temperature it is desired to measure. Barus' arrangement seems to be theoretically entirely satisfactory, but it is quite complicated and costly. One can still make use of muffles completely surrounded with flames, as in the fabrication of porcelain; the temperature there is very uniform. But their use offers a serious practical difficulty: the stem of the pyrometer, although well protected, frequently breaks at the point where it passes through the compartment of flames.

It will be more practical, perhaps, to make use of liquid baths—non-volatile fused salts for example, kept in continuous agitation, in which plunge at the same time the thermometer bulb and the body whose temperature is to be found, the heating being obtained by the combustion of gas in a Perrot furnace, or by an electric current passing through a coil immersed in the bath.

If one has to use an ordinary gas-furnace, Perrot furnace, or, better, a Leger furnace, it will be necessary to explore by means of a thermoelectric couple the distribution of temperature in the whole region utilized.

Satisfactory and uniform heating of a gas thermometer at high temperatures is secured only by the immersion of the bulb in an electrically heated furnace, the windings of which, preferably of platinum foil, are so spaced as to secure uniformity of temperature.

Industrial Air-pyrometers.—There have been attempts to construct air-thermometers suitable for industrial usage, the argument sometimes being advanced that a gas-pyrometer is *per se* better than any other. As we have seen, however, there is probably no physical instrument which is more difficult to employ satisfactorily, and any seeming gain in making direct use of an air thermometer for industrial use is wholly illusory. Other evident objections are fragility, uncertain correction due to the waste space, and the development of small and often unperceived leaks. Furthermore an empirical calibration is necessary so that such an instrument does not carry the gas-scale about with itself.

Among the instruments that have been considerably used is Wiborgh's air-pyrometer, shown in Fig. 9. A lens-

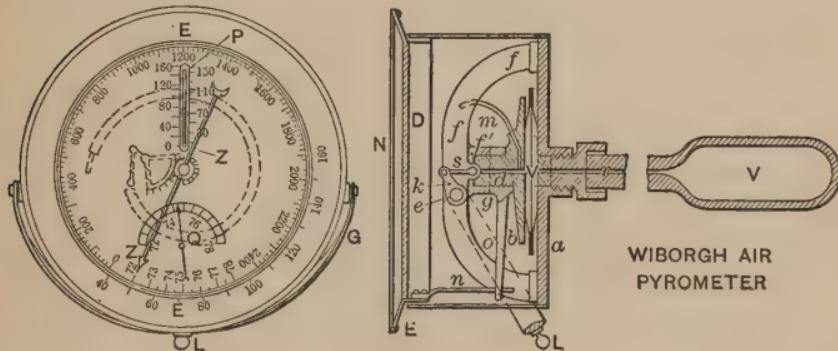


FIG. 9.

shaped V' reservoir is open to the air before an observation is taken, but when a temperature is to be read this lens is closed to the outer air and collapsed by a lever L , thus adding a definite mass of air to the bulb V of the thermometer; the resulting pressure is transmitted to a dial as in an aneroid barometer; provision is made for automatically correcting for variations in the pressure and temperature of the atmosphere.

INDIRECT PROCESSES.

We shall place in this list various experiments in which the laws of the expansion of gases have been used only in an indirect way, or have been extended to vapors.

Method of Crafts and Meier.—It is a variation of the method of H. Sainte-Claire-Deville and Troost, consisting in removing the gas by means of a vacuum. Crafts and Meier displaced the gas of the pyrometer by carbonic acid or hydrochloric acid, gases easily absorbable by suitable reagents. Hydrochloric acid is the more convenient, for its absorption by water is immediate; but there is to be feared at high temperatures its action on the air with formation of chlorine; it is preferable to employ nitrogen in place of air.

The apparatus (Fig. 10) consists of a porcelain bulb, whose inlet is large enough to let pass the entrance-tube of the gas, which reaches to the bottom of the bulb. This arrangement increases considerably the influence of the waste space and consequently diminishes the precision of the determinations.

This method is especially convenient for observations on the densities of vapors which are made by the same apparatus; it then allows of having an approximate idea of the temperatures at which the experiments are made.

Crafts and Meier have in this way determined the variations in density of iodine vapor as a function of the temperature.

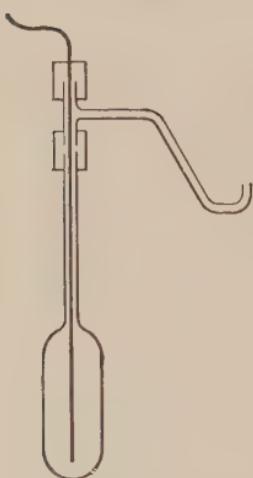


FIG. 10.

Regnault had previously proposed a similar method, without, however, making use of it.

1. One fills with hydrogen an iron vessel brought to the temperature that one desires to measure, and the hydrogen is driven out by a current of air; at the outlet of the metallic reservoir the hydrogen passes over a length of red-hot copper, and the water formed is absorbed in tubes of sulphuric acid in pumice-stone and weighed. This method, very complicated, is bad on account of the permeability of the iron at high temperatures.

At the same time, he proposed the following method:

2. An iron bottle containing mercury is taken; the vessel, being incompletely closed, is heated to the desired temperature and then allowed to cool, and the remaining mercury is weighed. This method is also defective on account of the permeability of iron at high temperatures; the hydrogen of the furnace-gases can penetrate to the inside of the recipient and drive out an equivalent quantity of mercury-vapor.

Methods of H. Sainte-Claire-Deville. — 1. This savant tried in the first place to measure temperature by a process analogous to that of Dumas' determination of vapor-densities. He took a porcelain bulb full of air, and heated it in the enclosure whose temperature was wanted, and sealed it off by the oxyhydrogen flame. He measured the air remaining by opening the bulb under water and weighing the water that entered, or else he determined merely the loss in weight of the bulb before and after heating.

Observations taken on the boiling-point of cadmium gave 860° . The data for the computation were as follows:

$$H = 766.4 \text{ mm.}$$

$$\text{Volume of bulb.} \quad = 285 \text{ cc.}$$

$$\text{Volume of remaining air} = 72 \text{ cc.}$$

The computation may be made also in this way: Let 17° be the surrounding temperature; $T_0=273^\circ+17^\circ=290^\circ$.

$$T'=290 \times \frac{285}{72} = 1150^\circ.$$

The correction due to the expansion of the porcelain is

$$0.0000135 \times 850 = 13^\circ,$$

which gives for the temperature of boiling cadmium

$$t=1150^\circ-273^\circ-13^\circ=864^\circ.*$$

The figure 860° is too high. There are in these experiments two possible sources of error: non-uniform heating on account of radiation, and the possibility of the existence of water-vapor in the bulb.

Besides, the small weight of the air and the difficulty of closing the recipient absolutely tightly render the experiments very delicate.

2. In a second method, which has the advantage of replacing the air by a very heavy vapor, Deville returned to the idea of Regnault, consisting in utilizing the vapor of mercury; but he ran against a practical difficulty. He had replaced the permeable iron recipients by porcelain recipients; the mercury condensed in the neck of the pyrometer and fell back in cold drops which caused the bulb to break.

* This result differs slightly from that given by Sainte-Claire-Deville, because we have taken as coefficient of expansion of porcelain the most recently obtained value; besides, the assumed temperature of the surroundings, 17° , differs perhaps from the real one, which is not given.

For this reason he abandoned mercury and replaced it with iodine; the return of a cold liquid was completely obviated by reason of the nearness of the boiling-point of this substance (175°) and its fusing-point (113°). A large number of observations were made by this method; the boiling-point of zinc, for example, was found to be equal to 1039° .

The data were:

$$H = 758.22 \text{ mm.}$$

$$\text{Volume of bulb.} \dots \dots \dots = 277 \text{ cc.}$$

$$\text{Increase in weight. Iodine-air.} \dots = 0.299 \text{ grm.}$$

$$\text{Volume of remaining air.} \dots \dots \dots = 2.16 \text{ cc.}$$

$$\text{Density of iodine-vapor.} \dots \dots \dots = 8.716$$

The computation can be made in the following way:

If the temperature of the surroundings is 17° , the theoretical weight of the iodine-vapor contained in the bulb at this temperature would be

$$1.293 \times 8.716 \times 0.277 \times \frac{273}{290} = 2.92 \text{ grms.}$$

The weight of iodine remaining in the reservoir is, taking note of the correction to be made resulting from the 2.16 grms. air which occupy 8.9 cc. at 930° ,

$$0.299 + 1.293(0.277 - 0.00216) \frac{273}{290} = 0.634 \text{ grm.}$$

If there had been no air, the weight would have been

$$0.634 \times \frac{277 + 8.9}{277} = 0.652 \text{ grm.}$$

$$\frac{T'}{T_0} = \frac{2.920}{0.652},$$

$$T' = 1290^{\circ}.$$

Making the correction for the expansion of porcelain (15°), we have

$$T' = 1290 - 273 - 15 = 1002^{\circ}.$$

The difference between the result of this computation and that of Deville comes from similar reasons to those noted above (page 84, note).

This method is quite faulty, as the iodine does not obey the laws of Mariotte and Gay-Lussac. The vapor-density of this substance decreases with rise of temperature, this effect being attributed to a doubling of the iodine molecule. This fact was established by Crafts and Meier and confirmed by Troost.

Temperatures.	445°	850°	1030°	1275°	1390°
Densities.	8.75	8.08	7	5.76	5.30
$\frac{D_t}{D_{445}}$	1	0.92	0.80	0.66	0.66

Troost found 5.70 at the temperature of 1240° .

If, in the preceding computation, we take 7.8 as the density of iodine at the boiling-point of zinc, we then find a temperature lower than 150° , which is far too low.

Method of Daniel Berthelot.—All the preceding methods are limited by the impossibility of realizing solid envelopes resisting temperatures higher than 1500° . D. Berthelot has devised a method which, at least in theory, may be applied to any temperatures, however high, because there is no envelope for the gas, or at least no envelope at the same temperature. It is based on the variation of the index of refraction of gaseous mass heated at constant pressure; the velocity of light depends upon the chemical nature and the density of this medium, but is independent of its physical state. A gas, a liquid, or a solid of the

same chemical nature produces a retardation of the light dependent only upon the quantity of matter traversed; this law, sensibly true for any bodies whatever, should be rigorously exact for substances approaching the condition of perfect gases. This retardation is measured by the displacement of interference fringes between two beams of parallel light, the one passing through the cold gas, the other through the hot gas. In reality Berthelot employs a null method; he annuls the displacement of the fringes in changing at constant temperature the pressure of the cold gas until its density is equal to that of the gas in the warm arm which is at constant pressure.

Apparatus.—There is a difficulty arising from the necessity of separating the light into two parallel beams, then reuniting them without imparting a difference of phase

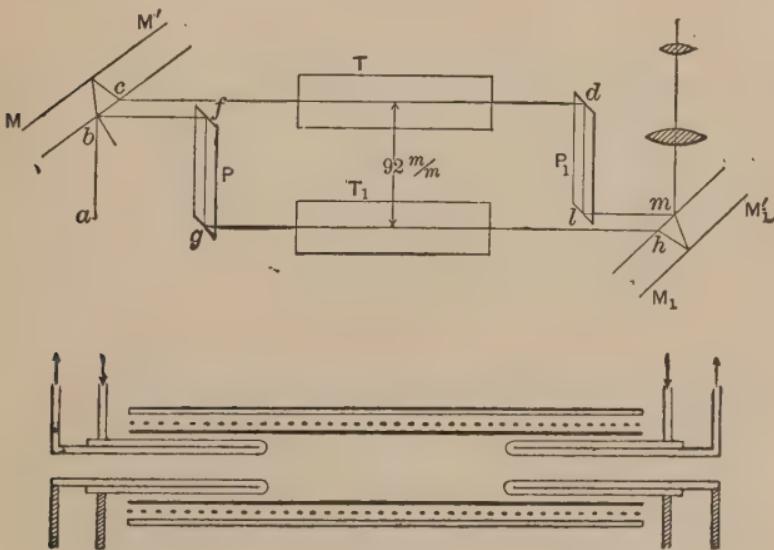


FIG. 11.

which renders the fringes invisible with white light. This is done in the following way (see Fig. 11);

A beam of light ab falls on a mirror MM' , which breaks it up into two parallel beams, bf and cd ; in order to separate the beams so as to be able to place apparatus conveniently with respect to them, a prism P gives to the beam bf the direction gh ; one can thus secure a separation of 92 mm. A second prism P_1 brings the beam cd into lm , and after reflection from a second mirror, M_1M_1' , the fringes are observed in a telescope focussed for parallel rays. The tubes containing the gases are placed at T and T_1 .

It is evidently necessary that the prisms P and P_1 be perfectly made. A preliminary adjustment is made with yellow light, then it is perfected with white light.

The tube at variable pressure is closed by two pieces of plate glass, as is also the warm tube; these four plates should be absolutely alike. The warm tube is heated by a vapor-bath at low temperatures, by an electric current passing through a spiral at high temperatures.

But there is a difficulty in that in the warm tube there exists a region of variable temperature between the warm zone and the cold atmosphere.

To eliminate the influence of this variable zone there are inside the warm tube two tubes containing running cold water whose distance apart can be changed; it is assumed that the variable region remains the same, and that distance between the two tubes gives the warm column actually utilized. It follows that the comparative lengths of the warm column and of the cold column (this latter remaining constant) are not the same; the formula to be used will be somewhat more complicated.

n being the index of refraction of a gas and d its density, we have

$$n-1=kd.$$

In the constant-pressure tube

$$\frac{d_1}{d_0} = \frac{p}{p_0}.$$

To obtain the invariability of the fringes it is necessary that

$$(n_1 - n_0)L = (n' - n_0)l,$$

L being the length of the cold tube, and l the displacement of the warm tube;

$$k(d_1 - d_0)L = k(d' - d_0)l,$$

$$L \left(\frac{d_1}{d_0} - 1 \right) = l \left(\frac{d'}{d_0} - 1 \right),$$

$$L \left(\frac{p}{p_0} - 1 \right) = l \left(\frac{T_0}{T} - 1 \right),$$

an expression which gives a relation between the pressures and the temperatures.

This method, employed for the control of the boiling-points, has given the following results, which are near those calculated from the old experiments of Regnault:

	Pressure.	Temperature Observed.	Temperature Calculated.
Alcohol.....	741.5 mm.	77°.69	77°.64
Water.....	740.1	99 .2	99 .20
“	761.04	100 .01	100 .01
Aniline.	746.48	183 .62	183 .54
“	760.91	184 .5	184 .28

Berthelot has standardized by the same method a couple which he used to determine the fusing-points of silver, copper, gold, and the boiling-point of zinc;

Silver.	962°
Gold.	1064
Zinc.	920
Cadmium.	778

The numbers found are nearly identical with those which result from the best determinations made by other methods.

We shall further discuss the determinations of fixed points in pyrometry in Chapter XIII.

CHAPTER IV.

CALORIMETRIC PYROMETRY.

Principle.—A mass p of a body, brought to a temperature T , is dropped into a calorimeter containing water at a temperature t_0 . Let t_1 be the final temperature of water and substance. P being the water-equivalent of the substances in contact (water, calorimetric vessel, thermometer, etc.) which are raised from t_0 to t_1 , L_t^T the heat required to warm unit mass of the body from t_1 to T , we have

$$L_t^T \times p = P(t_1 - t_0).$$

Taking as origin of temperatures the zero of the centigrade thermometer, the heat required to warm unit mass of the body to the temperature T will be

$$L_t^T = L_{t_1}^T + L_0^t.$$

The quantity L_0^t is easy to calculate, because the specific heats at low temperatures are sufficiently well known:

$$L_0^t = ct_1.$$

The expression for the total heat becomes

$$L_0^T \frac{P(t_1 - t_0)}{p} + ct_1.$$

t_1 and t_0 are the temperatures given by the direct readings of the thermometer.

The value of the second member is thus wholly known, and consequently that of the first member which is equal

to it. If previous experiments have made known the value of the total heat L_0^T for different temperatures, one may from the knowledge of L_0^T determine the value of T . It will be sufficient to trace a curve on a large scale whose abscissas are temperatures, and ordinates total heats, and to find upon this curve the point whose abscissa has the value given by the calorimetric experiment.

Choice of Metal.—Three metals have been proposed: *platinum, iron, and nickel*.

Platinum.—This metal was first proposed by Pouillet, and taken up again by Violle. It is much to be preferred to the other metals; its total heat has been compared directly with the indications of the air-thermometer. This metal can probably be reproduced identical with itself. Iridium, which commercial platinum often carries, has the same specific heat. The high price of these substances is an obstacle to their use extensively in works; for a calorimeter of a liter it is necessary to have at least 100 grms. of platinum,—or \$100 in a volume of 5 cc.,—easily lost or made away with.

Violle determined the total heat of platinum from 0° to 1200° , and computed by extrapolation up to 1800° .

100°.....	3.23 cal.	1000°.....	37.70 cal.
200	6.58	1100	42.13
300	9.75	1200	46.65
400	13.64	1300	51.35
500	17.35	1400	56.14
600	21.18	1500	61.05
700	25.13	1600	66.08
800	29.20	1700	71.23
900	33.39	1800	76.50

Iron.—Regnault, in a study made for the Paris Gas Company, had proposed, and caused to be adopted, iron, in attributing to it a specific heat of 0.126, while it is, at 0° , 0.106. He used a cube of 7 cm. sides which was thrust

into the furnaces by means of long iron bars. The calorimeter was of wood and had a capacity of 4 liters.

Various observers have determined the total heat of iron: at high temperatures the accord is not perfect among the results.

Temperature.	Post	Pionchon.	Euchène.	Mean Specific Heat.
Degrees.	Calories.	Calories.	Calories	Calories.
100	10.8	11.0	11.0	10.8
200	22.0	22.5	23.0	21.5
300	35.0	36.5	37.0	32.5
400	39.5	41.5	42.0	43.0
500	67.5	68.5	69.5	54.0
600	86.0	87.5	84.0	65.0
700	108.0	111.5	106.0	76.0
800	132.0	137.0	131.0	87.0
900	157.0	157.5	151.5	98.0
1000	187.5	179.0	173.0	109.0

But this metal is not at all suitable for such use, by reason in the first place of its great oxidability. There is formed at each heating a coating of oxide which breaks off upon immersion in water, so that the mass of the metal varies from one observation to the next. Besides, iron, especially when it contains carbon, possesses changes of state accompanied during the heating by a marked absorption of heat. By cooling in water, hardening takes place which may irregularly prevent the inverse transformations. The use of electrolytic iron is therefore preferable.

Nickel.—At the Industrial Gas Congress in 1889 Le Chatelier proposed nickel, which is but slightly oxidizable up to 1000°, and which above 400° does not possess changes of state as does iron.

The total heat of nickel has been determined by Pionchon and by Euchène and Biju-Duval.

The differences are due very probably in part to impurities that the nickel may contain.

Temperature.	Pionchon.	Euchène.
Degrees.	Calories.	Calories.
100	11.0	12.0
200	22.5	24.0
300	42.0	37.0
400	52.0	50.0
500	65.5	63.5
600	78.5	75.0
700	92.5	90.0
800	107.0	103.0
900	123.0	117.5
1000	138.5	134.0

Calorimeters.—1. In laboratories there is employed with the platinum mass Berthelot's calorimeter, a description of which is given in the *Annales de Chemie et de Physique* * (Fig. 12). The thermometer used for the measurement

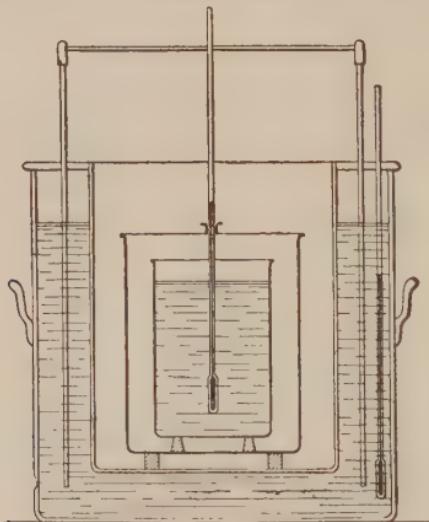


FIG. 12.

of the rise in temperature should be very sensitive, so that a rise of from 2° to 4° be sufficient in order to render

* 4th Series, t. xxix. p. 109; 5th Series, t. v. p. 5; t. x. p. 433 and 447; t. xii. p. 550.

negligible the cooling correction. If use is made, for instance, of a thermometer giving the hundredth of a degree, the mass of platinum should be about one-twentieth the mass of the water in the calorimeter.

2. In the arts, where the measurements are made with less precision, and where it is necessary to consider the cost of installation of the apparatus, nickel will be made use of, a thermometer giving tenths of a degree, and a zinc calorimeter, which may be home-made. Such an installation may cost as little as \$4. A mass of nickel should be used equal to one-twentieth of the mass of water of the calorimeter.

The calorimeters used by the Paris Gas Company are after the Berthelot pattern. They are also water-jacketed calorimeters, of which there are two types.

Water-jacketed Calorimeters (Figs. 13 and 14).—These

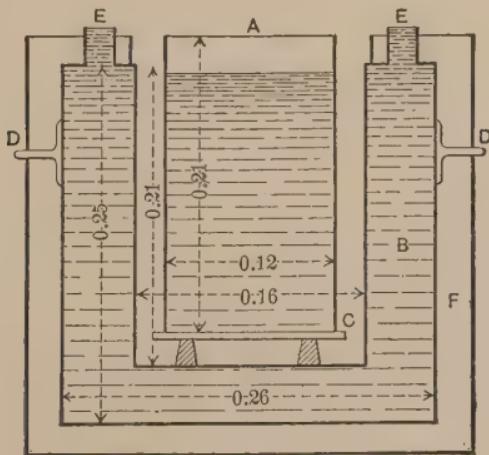


FIG. 13.

A, cylindrical vessel of thin copper; *B*, water-jacket; *C*, wooden support; *D*, handles; *E*, filling-tubes; *F*, felt jacketing.

apparatus consist of a cylindrical calorimeter of two liters capacity, of zinc or of copper; a double cylindrical jacket

of the same metal, containing water and surrounded by felt on the outside. The calorimeter rests on this jacket by means of a wooden support. A thermometer graduated

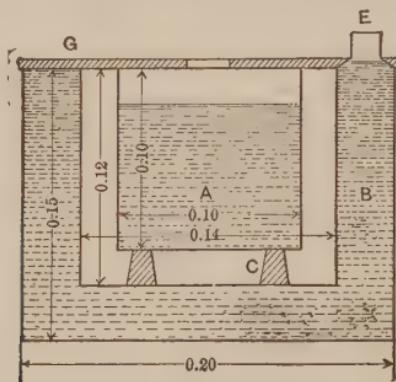


FIG. 14.

A, zinc vessel; B, water-jacket; C, cork supports; E, filling-tube; G, cardboard cover.

to fifths of a degree, having a small but quite long bulb, serves as stirrer. The thermometric substance is a piece of nickel of mass equal to one-tenth that of the water, or 200 grms., so as to have considerable rise of temperature easy to read by the workmen who make the measurements.

As a general rule, one must avoid placing the thermometric substance upon the floor of the furnace. The piece of nickel, which is made in the form of small cylinders having from 15 to 25 mm. diameter and from 10 to 30 mm. length, rests so as to be insulated from the floor in a nickel crucible provided with a foot and with

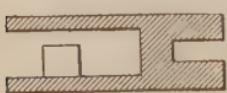


FIG. 15.

two arms attached somewhat above the centre of gravity. When it has been heated for a half-hour an observer takes out the crucible with a forked rod, and another seizes this crucible with tongs to empty it into the calorimeter.

Another method of heating the calorimeter is to surround it with a furnace, the temperature of which is to be determined by a thermometer placed in the furnace. The furnace is made of a

Use is not made of an iron crucible because this metal oxidizes and lets drop scales, which falling into the calorimeter would vitiate the experiment. Fig. 15 shows the arrangement of such a crucible containing a nickel cylinder.

Siemens Calorimeter. — A convenient form of direct-reading calorimeter due to Siemens is shown in Fig. 16. Using always the same mass of water and a ball of given mass and kind, the thermometer may be graduated to read directly the temperature attained by the heated ball.

Precision of the Measurements. — Biju-Duval has made a series of experiments to study the sources of error arising from the use of the calorimeter by comparing its indications to those of the thermo-electric pyrometer of Le Chatelier. The observations were taken by varying the following conditions:

Use of thermometer graduated to $1/5^{\circ}$ or to $1/50^{\circ}$.

Use of the old wooden gas-works calorimeter or of the water-jacketed calorimeter.

Use of iron or nickel.

I. Experiment. — Old wooden gas-works calorimeter. Iron. Thermometer in fifths.

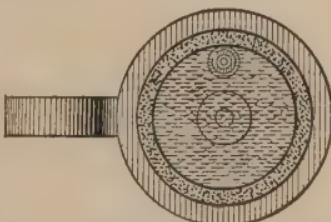
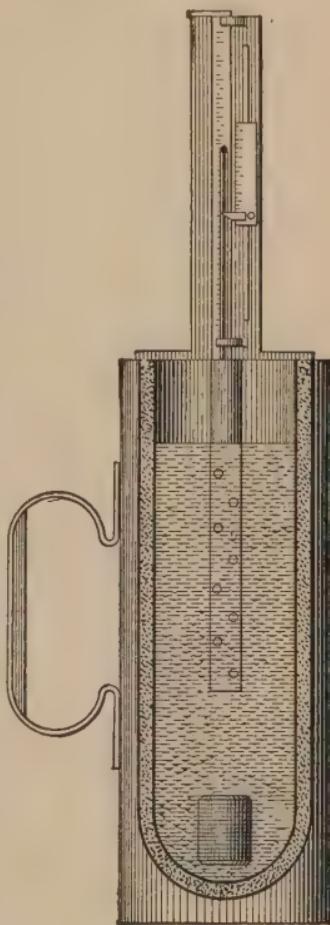


FIG. 16.

$$P = 10000 \text{ grm.}$$

$$p = 1031 \text{ "}$$

$$t_0 = 20^\circ.8$$

$$t_1 = 36^\circ.2$$

$$Q_0^T = 153.5 \text{ cal.}$$

Computed temperature:

$$\text{Mean specific heat of iron} = 0.108 \quad t = 1420^\circ$$

$$\text{“ “ “ “ “} = 0.126 \quad t = 1210$$

$$\text{Total heat according to Biju-Duval} = 915$$

$$\text{Thermoelectric pyrometer} = 970$$

It is thus evident that the mean specific heats even with the correction suggested by Regnault give temperatures much too high. With the curve of total heats the temperature found is much too low on account of the following losses of heat:

1. Absorption of heat by the wooden walls;
2. Radiation from the iron cube during transfer;
3. Cooling of the water in the calorimeter, whose temperature exceeded by 16° the temperature of the surroundings.

The following experiments were made with the thermometer reading to $1/50^\circ$; the piece of nickel was protected against radiation by a crucible. The two calorimeters were compared.

II. Trial with the Wooden Calorimeter.

$$T = 975^\circ \text{ by the thermoelectric pyrometer}$$

$$P = 10000 \text{ grm.}$$

$$p = 145 \text{ "}$$

$$t_0 = 20^\circ.21$$

$$t_1 = 21^\circ.99$$

$$L_0^T = 125 \text{ cal.}$$

$$L_0^T = 130 \text{ cal. from the curve at } 975^\circ$$

The difference is 5 calories, or 4 per cent loss due to the jacket.

III. Trial with the Water-jacketed Calorimeter.

$$T = 985^\circ$$

$$P = 2000 \text{ grm.}$$

$$p = 48.4 \quad "$$

$$t_0 = 18^\circ.86$$

$$t_1 = 21^\circ.95$$

$$L_0^T = 130 \text{ cal.}$$

$$L_0^T = 131.5 \text{ cal. from the curve at } 985^\circ$$

The difference is 1.5 calories, or a loss of only 1.11 per cent when use is made of a carefully made calorimeter and of a thermometer giving $1/_{50}^\circ$. This corresponds to an uncertainty of less than 10° in the temperatures sought. With the $1/_{10}^\circ$ thermometers, necessitating a much greater rise of temperature of the water in the calorimeter, an uncertainty of 25° will exist.

Conditions of Use.—The advantages of the calorimetric pyrometer are:

1. Its low net cost;
2. The ease of its use, which allows of putting it in the hands of a workman.

Its inconveniences are:

1. The time necessary to take an observation, about a half-hour; except with Siemens form.
2. The impossibility of taking continuous observations.
3. The impossibility of exceeding 1000° by the use of the piece of nickel.
4. The deterioration of the balls used due to oxidation.

Its use does not seem to be recommendable for laboratories.

It is to be recommended for works in the cases where it

is required to make only occasional measurements; in cases where there is not the personnel sufficiently skilful to use the more precise methods; and finally where the importance of the measurements is not such as to justify the buying of more costly instruments.

CHAPTER V.

ELECTRICAL RESISTANCE PYROMETER.

Principle.—In this apparatus use is made of the variations of electric resistance of a platinum wire as a function of the temperature; these variations are of the order of magnitude of those of the expansion of gases. The ratio of the resistances is 1.34 at 100°, and 4 at 1000°. As electric resistances are measurable with great accuracy, this process of estimation of temperatures offers a very great sensibility, and applying exactly the law that connects the variations of resistances to those of temperature most excellent results may be obtained.

The electric pyrometer was proposed by Siemens in 1871 (Bakerian Lecture); it rapidly came into use in metallurgical works on account of the reputation of its inventor, but it was soon abandoned for reasons which will be given later.

Investigations of Siemens.—The Siemens pyrometer consists of a fine platinum wire 1 m. long and 0.1 mm. in diameter, wound on a cylinder of porcelain or fire-clay; the whole is enclosed in an iron tube, destined to protect the instrument from the action of the flames.

Siemens tried also, but without success, ceramic matters impregnated with metals of the platinum group.

To measure resistance he employed either a galvanometer, for laboratory experiments, or a voltameter, for the measurement in works. In this latter case the current from a cell divides between the heated resistance and a

standard resistance at constant temperature; in each one of the circuits was placed a voltameter: the ratio of the volumes of gas set free gives the ratio of the current strengths and thus the inverse ratio of the resistances.

Finally Siemens gave a formula of three terms connecting the electrical resistance of platinum to temperatures on the air-thermometer, but without publishing the experimental data on which this graduation was based.

Experiment soon showed that the apparatus did not rest comparable with itself. A committee of the British Association for the Advancement of Science found that the resistance of platinum increases after heating. It would be necessary then to graduate the apparatus each time that it was used. This change of resistance is due to a chemical alteration of platinum, which is enormous when directly heated in the flame, less, but still marked, if placed in an iron tube, and which disappears if use is made of a platinum or porcelain tube. This augmentation of resistance may reach 15 per cent by repeated heatings up to 900°.

Platinum being very costly and porcelain very fragile, it was impossible to use these two bodies in the industries, which alone at that time occupied themselves with measurements of high temperatures, and this method was abandoned completely during twenty years.

Researches of Callendar and Griffiths.—These savants have revived this method for laboratory purposes; it seems the best for work of precision, on the condition of being assured of the invariability of the resistance of platinum.

Callendar found that clay helps to cause the variation of resistance, that the platinum wire becomes brittle on its support and sticks there; this action is probably due to impurities in the clay. With mica, on the other hand, which the wire touches only at the edges (the reel is made

of two perpendicular slices of mica), there is perfect insulation without cause of alteration; but mica becomes dehydrated at 800° and then becomes very fragile.

All metallic solderings should be proscribed, for they are volatile and attack platinum.

Pressure joints (screw or torsion) are equally bad, for they become loose. One should use only the "autogène" solder by the fusion of platinum.

Copper conductors should also be rejected, at least in the heated portions, on account of the volatility of the metal. A pyrometer with such conductors, heated during an hour at 850° , showed an increase of resistance of $\frac{1}{3}$ per cent.

Investigations of Holborn and Wien.—These savants have made a very complete study of this alterability of platinum wires, in a comparison between the methods of measurement of temperatures by electric resistance and thermoelectric forces; they worked with wires of 0.1 mm. to 0.3 mm. diameter. They soon found that above 1200° platinum commences to undergo a feeble volatilization which suffices to augment notably the resistance of the very fine wires. Hydrogen in presence of silicious matters causes at about 850° a rapid alteration of the platinum.

Below are the results relative to wires of 0.3 mm. of a length of 160 mm.

Wire α .	R at 15° .	Wire β .	R at 15° .
At start.....	0.239 ohm	At start.....	0.247 ohm
After heating red-hot:		After several days in }	
Twice in air at 1200°	0.238 "	hydrogen at 15°	0.246 "
Once in vacuo	0.240 "	After heating in hy-	
" " H	0.262 "	drogen to 1200°	0.255 "
" " vacuo	0.253 "		
Wire γ .			R at 15° .
At start.....			0.183 ohm
After heating in air to 1250° (three times)			0.182 "
" " " H " "		0.188 "
" " " " "		0.195 "

Wire γ heated to 1350° in an earthenware tube and in hydrogen became brittle; this result may be explained by a silicuration of the platinum, for there is nothing observed if the wire is heated by the electric current in the interior of a cold glass tube, even in hydrogen. Similar experiments were made by the same observers with palladium, rhodium, and iridium.

With palladium the absorption of hydrogen at low temperatures, giving the hydride, increases the resistance by 60 per cent; besides, the same effect of alteration as with platinum is noticed if the palladium is placed in hydrogen in presence of silicon.

There is no definite conclusion to be drawn from the experiments with rhodium and iridium, except that these metals assume their normal resistance only after having been heated several times to a high temperature.

Law of the Variation of Platinum Resistance.—Calendar and Griffiths have compared the resistance of platinum with the air-thermometer up to 550° ; they found that up to 500° the relation could be represented at least to $0^\circ.1$ by a parabolic formula of three parameters. In order to graduate such a pyrometer it would be sufficient then to have three fixed points: ice, water, sulphur.

They gave a special form to the relation; let p be the electric temperature defined by the relation

$$p_t = \frac{R_t - R_0}{R_{100} - R_0} \cdot 100,$$

that is to say, the value of the temperature in the case in which the resistance varies proportionally to the temperature.

They then placed

$$t - p_t = \delta \left[-\frac{t}{100} + \left(\frac{t}{100} \right)^2 \right].$$

It would appear as if this formula contained the single parameter δ ; but in reality p_t includes two.

Substituting for p its value, we have

$$R_t = R_0 t + \frac{(1 + \delta)(R_{100} - R_0)}{(100)^2} \cdot t - \delta \frac{R_{100} - R_0}{(100)^3} \cdot t^2,$$

an equation of the form

$$R_t = a + bt + ct^2.$$

This complicated form is without interest. Callendar and Griffiths used their pyrometer before having standardized it against the air-thermometer. Not being able to compute t , they provisionally computed the approximate temperatures p_t , and later determined the correction between t and p_t , after having sought the formula expressing the difference between these two quantities. By extrapolation up to 1000° the points of fusion of gold and of silver were found quite near to those determined by other observers.

Harker, working at the National Physical Laboratory, England, has recently compared the readings of platinum-thermometers, when reduced to the air-scale by the use of Callendar's difference formula, with the readings of thermocouples calibrated at the Reichsanstalt, and with the indications of an glazed porcelain-bulb nitrogen-thermometer at constant volume. Specially constructed, compensated electric furnaces were used for heating.

As shown by the table on p. 106, the agreement between the scales of the platinum-resistance and thermoelectric pyrometers was within 0°.5 C. throughout the temperature range up to 1000°, although the gas-pyrometer gave somewhat discordant results.

COMPARISONS OF PYROMETRIC SCALES.

Temperature.			G-Pt.	G-Th.	P-Th.
Gas-thermometer.	Thermo-couple.	Pt Thermometer.			
523.1	524.3	524.39	-1.3	-1.2	-0.1
598.5	597.8	597.62	+0.9	+0.7	-0.2
641.1	641.1	641.75	+0.6	+0.0	-0.6
776.7	775.5	775.13	+1.6	+1.2	-0.4
820.0	818.4	818.31	+1.7	+1.6	-0.1
875.0	875.4	875.24	-0.2	-0.4	-0.2
959.8	956.0	955.47	+4.3	+3.8	-0.5
1005.0	1004.4	1004.37	+0.6	+0.6	-0.0

These results confirm the view of the sufficiency of the difference formula for the most accurate work up to the upper limit of the safe use of the platinum-resistance thermometer.

Holborn and Wien have shown that at very high temperatures the interpolation formula is certainly inexact. The resistance seems to become asymptotic to a straight line, while the formula leads to a maximum evidently unacceptable; it would be without doubt better represented by an expression of the form

$$R \cdot t = a + b(t + 273)^m.$$

Here are the results of several experiments made on the same wire by these two savants:

<i>t.</i> Degrees.	<i>R.</i> Ohms.	<i>t.</i> Degrees.	<i>R.</i> Ohms.
0.	0.0355	0.	0.0356
1045.1510	1040.1487
1193.1595	1144.1574
1303.1699	1328.1720
1395.1787	1425.1802
1513.1877	1550.1908
1578.1933	1610.1962

This wire came in contact with the furnace-gases, as a result of breaking the tube, and was broken. Another wire gave the following results:

<i>t.</i>	<i>R.</i>
567°.....	0.0972 ω
7721164
10451408
11851511
12631573

Although the work of Holborn and Wien, as well as that of Tory and others, shows that the platinum-resistance thermometer cannot be depended upon above 1000° C., yet, in the range from -200° C. to +1000° C., it serves as the most accurate, and, on the whole, most convenient method of measuring temperatures where great precision is required, and is particularly adapted for the delicate control of a given temperature.

Nomenclature.—To determine a temperature by means of a platinum-thermometer, if the instrument has not been calibrated already in degrees, it is necessary to know the difference coefficient δ of the wire, which may be obtained by finding the platinum temperature pt at some known point as the sulphur boiling-point (S.B.P.), or by comparison with a calibrated instrument.

Callendar has suggested the following notation which seems convenient for platinum thermometry:

Fundamental Interval.—The denominator $R_{100} - R_0$ in the formula

$$pt = 100(R - R_0)/(R_{100} - R_0), \dots \quad (1)$$

for the platinum temperature pt , represents the change of resistance of the thermometer between 0° and 100°.

Fundamental Coefficient = c = mean value of tempera-

ture coefficient of change of resistance between 0° and 100°:

$$c = (R_{100} - R_0) / 100R_0.$$

Fundamental Zero = $pt_0 = \frac{1}{c}$ = reciprocal of fundamental coefficient. It represents the temperature on the scale of the instrument itself at which its resistance would vanish.

Difference Formula.—The following form is the most convenient for computation:

$$D = t - pt = \delta \cdot (t/100 - 1) \cdot t/100. \dots \quad (2)$$

Parabolic Function expresses the vanishing at 0° and 100° of above formula, which becomes

$$t = pt + \delta \cdot p(t).$$

“*S.B.P.*” *Method of Reduction*.— D is obtained very conveniently by determining R'' , and thus pt'' at t'' = the boiling-point of sulphur.

Resistance Formula.—The parabolic difference formula is equivalent to assuming

$$R/R_0 = 1 + at + bt^2, \dots \dots \dots \quad (3)$$

where

$$a = c(1 + \delta/100), \quad b = -c\delta/10000.$$

Graphic Method of Reduction.—The easiest way to reduce platinum temperatures to the gas-scale is to plot the difference $t - pt$ in terms of t as abscissas, and to deduce graphically the curve of difference in terms of pt as abscissas. This is most convenient for a single instrument up to 500°.

Other methods have been used by Heycock and Neville and by Tory.

Difference Formula in Terms of pt :

$$t - pt = d'(pt/100 - 1)pt/100 = d'p(pt). \dots \quad (4)$$

This formula is to be used only where a high degree of accuracy is not required. The value of d' may be determined from S.B.P., or approximately

$$d' = \delta / (1 - 0.077\delta).$$

Dickson has proposed the formula

$$(R + a)^2 = p(t + b),$$

which agrees with (3) over a very wide range in the case of platinum. It has the possible theoretical advantage of not requiring a maximum value for the resistance of platinum. This form, however, does not lend itself to the convenient graphical treatment applicable to the difference formula.

There is advantage in using the silver fusing-point in calculating the value δ for impure wires that are to be used at high temperatures. For the whole range of temperatures with such a wire both the sulphur and silver points may be obtained, when δ takes the form $a + bt$.

The platinum-thermometer may be, and should be, for practical work, constructed so as to read directly in platinum degrees. This method saves much time and chance of error. The calibration curve once made for a given instrument serves indefinitely, so that, in spite of the appearance of complications in the method, actually in practical use the determination of a temperature on the normal scale by the platinum-thermometer is the affair of a few seconds only.

Use as a Standard.—A very careful comparison of the reduced indications of several platinum-thermometers with the gas-scale as furnished by a constant-volume nitrogen-thermometer has been made recently by Chappuis and Harker at the International Bureau at Sèvres, and their results confirm those of Callendar: that the indications of the platinum-thermometer up to 600° C. can be sufficiently well expressed by Callendar's formula.

In view of the relative ease and great precision of the resistance measurements and the great difficulties in the use of the gas-thermometer, Callendar has suggested that the platinum-thermometer be adopted as a secondary standard, reducing its readings as above indicated, assuming as calibration-points 0°, 100°, 444°.5, the last being the sulphur boiling-point on the constant-pressure scale. All platinum-thermometers could then be compared with one selected as standard and calibrated as above indicated. With regard to portability and ease of reproduction, it is sufficient to send a few grammes of the standard wire in an ordinary letter, to reproduce the scale with the utmost accuracy in any part of the world.

Experimental Arrangements (Fig. 17).—In Callendar's pyrometer the platinum wire is wound on two strips of



FIG. 17.

mica set crosswise. Four heavy platinum wires serve to lead in and out the current; two of them are to compensate for the influence of temperature along the parallel conductors.

In the laboratory the resistance measurements are made by a Wheatstone bridge (Fig. 18). A resistance-box is used, furnished also with a rheostat consisting of a stretched platinum wire serving to measure the small fractions of resistance.

In industrial practice use is made of an apparatus (Fig. 19) composed of a needle-galvanometer and a resistance-

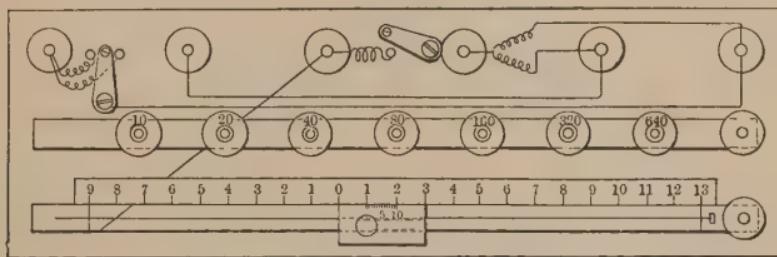


FIG. 18.

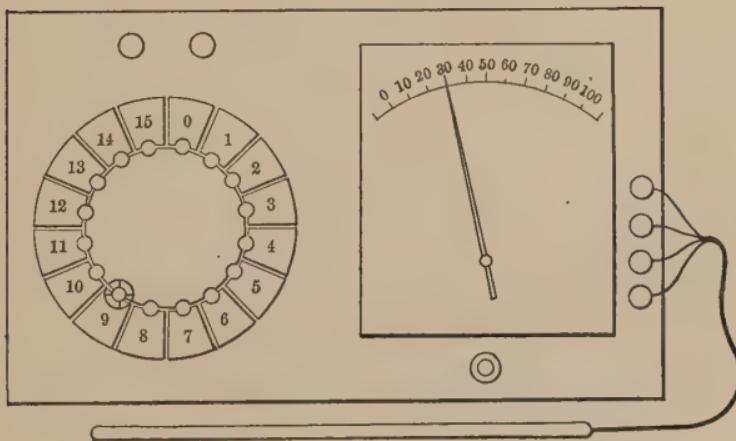


FIG. 19.

box of circular form, consisting of fifteen spools of 1 ohm. The deflection corresponding to two successive contacts is read, and by interpolation is found the real value of the resistance. The approximation thus obtained is sufficient.

Another form of direct-reading instrument, designed by Mr. Whipple of the Cambridge Scientific Instrument Co., is shown in Fig. 20. This instrument is portable, direct-reading, and requires no especial skill to use it.

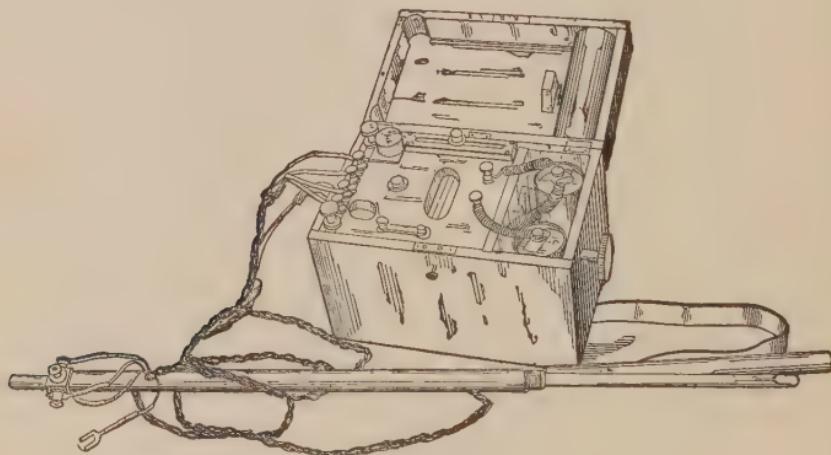


FIG. 20.

To avoid breaking, the pyrometer should be installed in advance in the cold furnace, or heated previously in a muffle if it is necessary to introduce it into the hot furnace. It is necessary to take care and heat the porcelain throughout sufficient of its length in order to avoid the effect of the interior conductibility, which would prevent the spiral taking the temperature of the surrounding medium.

Some Results Obtained.—Callendar and Griffiths have determined a certain number of fusing- and boiling-points:

Fusion.	Ebullition under 760 mm.
Tin.	232°
Bismuth.	270
Cadmium.	322
Lead.	329
Zinc.	421
Aniline.	184°. 1
Naphthaline.	217 . 8
Benzophenone.	305 . 8
Mercury.	356 . 7
Sulphur.	444 . 5

We may compare these results with the anterior determinations of Crafts with the air-thermometer:

Naphthaline.		Benzophenone.	
<i>p.</i> Millimeters.	<i>t.</i> Degrees.	<i>p.</i> Millimeters.	<i>t.</i> Degrees.
730.3	216.3	730.9	304.2
740.3	216.9	740.1	304.8
750.5	217.5	750.9	305.5
760.7	218	760.3	306.1

Regnault had found for mercury:

$t=350^{\circ}$ under a pressure of	663 mm.
$t=360$ " " "	797.7 "
$t=370$ " " "	954.6 "

Heycock and Neville have applied the method previously described, in prolonging the graduations, by extrapolation, to the determination of the fusing-points of several metals and salts:

Metals .	Tin	232°
	Zinc.	419
	Magnesium (1 per 100 of impurities) . . .	633
	Antimony.	629.5
	Aluminium (0.5 per 100 of impurities) . . .	654.5
	Silver.	960.5
	Gold.	1062
Salts . .	Copper.	1080.5
	Potassium sulphate	{ 1084° (fusion) 1067 (solidification)
	Sodium sulphate.	{ 902 (fusion) 883 (solidification)
	Sodium carbonate.	850

The difference found between the points of fusion and of solidification of potassium sulphate is explained by the presence of a dimorphic point of transition in the neighborhood of the fusing-point. It is a case analogous to that

of sulphur; there is observed, according to the case, the point of fusion or solidification of the one or the other dimorphic variety. It is without doubt the same in the case of the sodium sulphate.

Sources of Error.—*Heating of Thermometers by the Measuring Current.*—It is evident that if a too large current is sent through an electrical-resistance thermometer, the heating thus occasioned will cause the indicated temperatures to be high. The limiting value of the current Callendar has shown to be about 0.01 ampere per 0.01 degree with an average platinum-thermometer of wire 0.15 mm. in diameter. If a galvanometer of sufficient sensibility is used this effect is negligible, and when a greater current has to be used on account of lack of galvanometer sensibility, the heating effect may be maintained nearly constant by keeping the current constant by means of a rheostat in the battery circuit, since the resistance of the thermometer increases very nearly as fast as the rate of cooling, or a little faster than the temperature. Callendar also indicates that the heating effect is readily measured by using as current-source two storage cells, connected first in parallel and then in series, the current heating correction being given by subtracting from the first reading one-third of the difference between the two readings.

Lag of the Platinum-thermometer.—Enclosed as it necessarily is for most work in a sheath of porcelain and possessing besides considerable mass, the platinum-thermometer does not immediately assume the temperature of its surroundings. Put into a sulphur bath it assumes an equilibrium condition in ten minutes. For small changes of temperature this effect is hardly perceptible and may be neglected in all practical work.

Insulation.—Defective insulation due to moisture condensed in the tubes is sometimes a source of error in

accurate work at the ice point and lower temperatures with thermometers of high resistance if the tubes are not sealed. This may be readily done if the containing sheath is of glass, by sealing the platinum leads into the glass so that they terminate in cups. When the containing sheath is of porcelain, as for high temperature work, this sealing is not necessary, nor is it possible, but running the leads into metal cups containing a fusible alloy still offers the readiest method of securing a good contact with the rest of the circuit.

Compensation for Resistance of the Leads.—It is necessary, in order to avoid thermal currents at the junctions with the thermometer proper and also evaporation and consequent change of resistance, to employ platinum leads from the thermometer to a point in the circuit at a constant temperature. These leads should be of relatively large size to keep their resistance as small as possible, but even then there will still remain an error due to the varying resistance of these leads with change in temperature and with varying depth of immersion. It becomes necessary either to apply a "stem correction," which is troublesome and uncertain, or compensate for this effect. Nowadays most platinum-thermometers sold are compensated.

This compensation is effected in either of two ways; in the first, when the platinum-thermometer PT forms one arm of a Wheatstone bridge (Fig. 21), the compensating leads A_1B_2 , of exactly the diameter and resistance of the thermometer leads C_1D_1 , are inserted in the balancing arm R of the bridge, so that the resistance of the thermometer remains apparently constant for any depth of immersion.

The second method of compensation is employed when the resistance of the thermometer is to be determined by means of a potentiometer and standard resistance

(Fig. 22). Potential leads, which may be of fine wire, are soldered to the terminals of the thermometer, and the measuring current being kept constant, the P.D. across the standard resistance and across the thermometer-coil are measured rapidly in succession by means of a

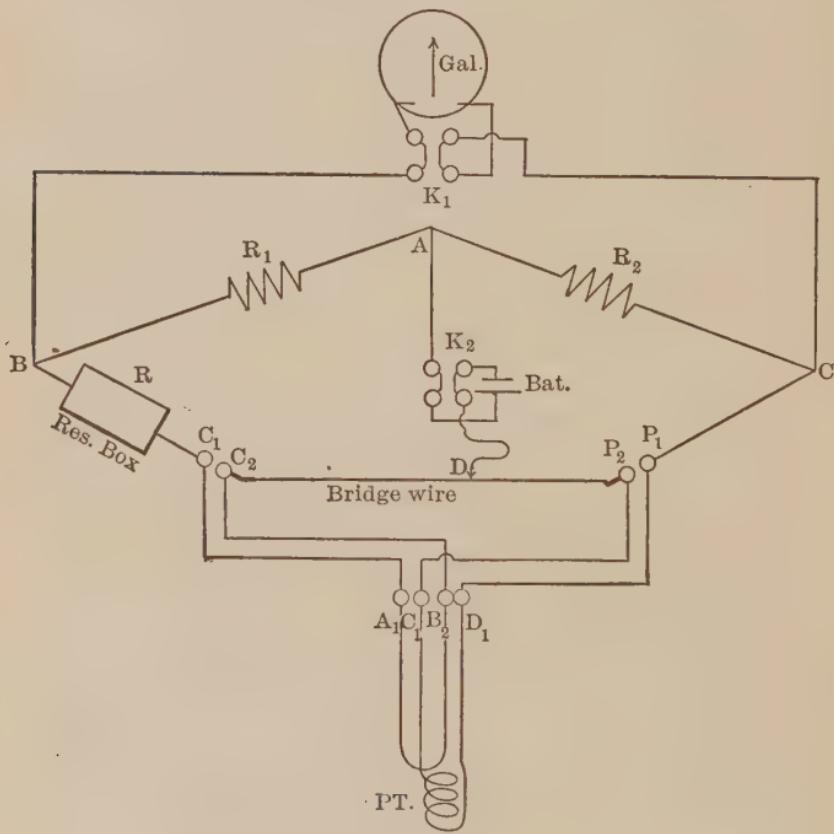


FIG. 21.

potentiometer (Fig. 23), thus giving directly the resistance of the thermometer-coil alone in terms of the standard resistance. Either of these methods of compensation and of resistance measurement is susceptible of great accuracy.

Pyrometers having Different Values of δ .—The value of

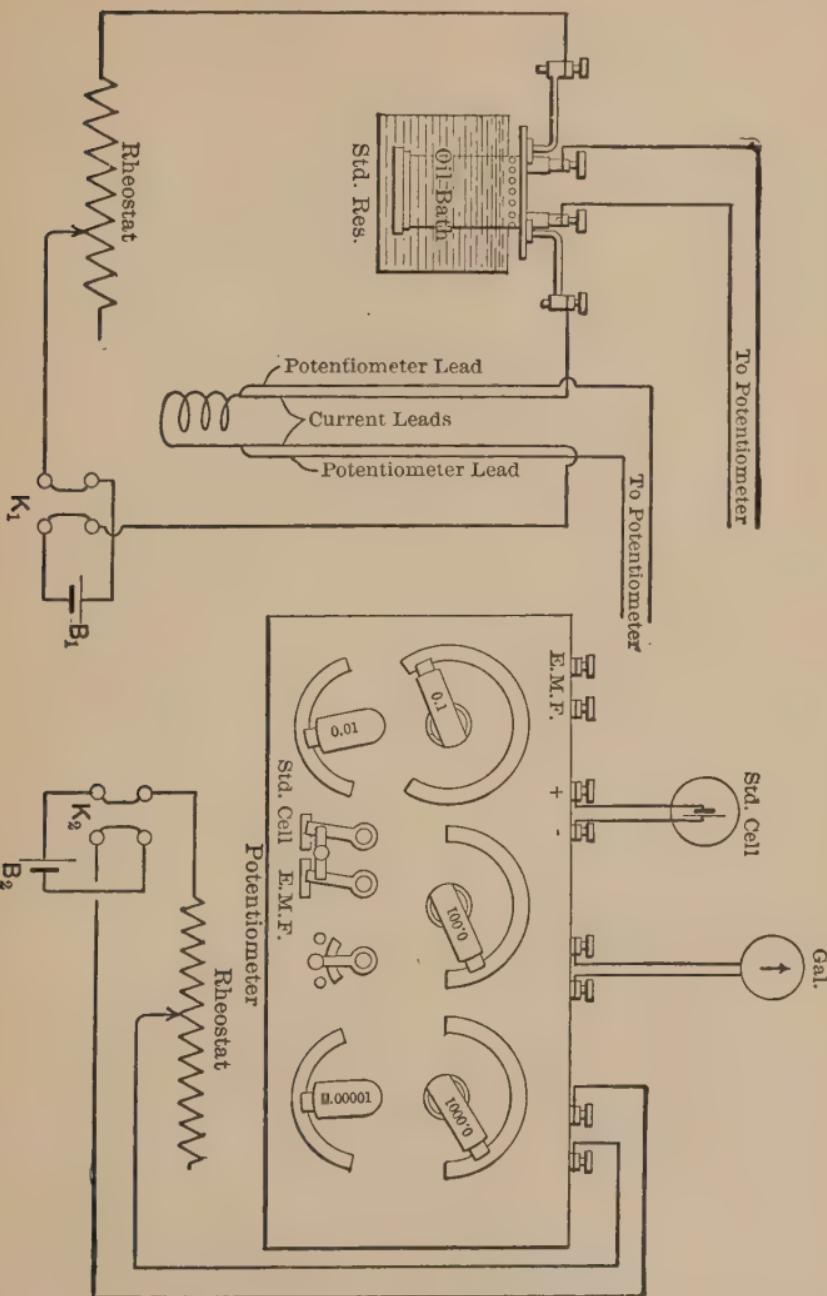


FIG. 22.

FIG. 23.

δ is a measure of the chemical properties alone of the platinum wire used, the pure metal having a value of very exactly $\delta = 1.500$ and impure metals giving greater values. It might be expected that thermometers having very different values of δ would give discordant results when reduced by the parabolic formula to the gas-scale. The work of Heycock and Neville shows, however, that such is not the case, as is indicated by the following observations on the freezing-point of gold:

Pyrometer.	δ	pt	t° C.
13	1.500	908.60	1061.8
16	1.532	906.56	1062.1
13A	1.553	905.8	1061.9
15	2.04	873.1	1061.2

Wires having a large δ are more liable to change with use, so that although correct results may be obtained with them if checked up occasionally, it is preferable to use the purest of platinum.

Changes in the Constants.—If platinum-thermometers are repeatedly heated to temperatures in the neighborhood of 1000° C., or are kept for very considerable periods of time at even lower temperatures, changes in the value of the constants R_0 , R_{100} , and δ will develop. Pyrometers for use at high temperatures should not be enclosed in inglazed porcelain even if the glaze does not touch the metal, as deterioration of the latter will otherwise ensue. The mica supports undergo distortion on cooling from high temperatures, increasing in size, tending to stretch the wire and increase its resistance. For this reason it is probably better to use the constants determined before a measurement at high temperature rather than those

determined afterwards. Again, if the wire of the thermometer has not been well annealed at a temperature higher than it is to be used, irregular changes will occur which are the most marked for the first few heatings.

Conditions of Use.—The electrical-resistance pyrometer seems, by reason of the great precision of the measurements which it allows, to be especially serviceable for laboratory investigations. It seems, on the other hand, to be too fragile for the greater part of the industrial applications, although it is very convenient in permanent installations when properly protected.

The relation between the platinum-thermometer scale and the gas-scale is fairly well established up to 1000° C., which is near the limit beyond which it is not safe to use this instrument without frequent checking of its calibration.

The resistance pyrometer is the best instrument for differential work and for detecting small temperature changes as well as for controlling a constant temperature. Great care has to be taken that the platinum does not become contaminated.

CHAPTER VI.

THERMOELECTRIC PYROMETER.

Principle.—The junction of two metals heated to a given temperature is the seat of an electromotive force which is a function of the temperature only, at least under certain conditions which we shall define further on. In a circuit including several different junctions at different temperatures the total electromotive force is equal to their algebraic sum. In a closed circuit there is produced a current equal to the quotient of this resultant electromotive force and the total resistance.

Experiments of Becquerel, Pouillet, and Regnault.—It was Becquerel who first had the idea to profit from the discovery of Seebeck to measure high temperatures (1830). He used a platinum-palladium couple, and estimated the temperature of the flame of an alcohol lamp, finding it equal to 135° . In reality the temperature of a wire heated in a flame is not that of the gases in combustion; it is inferior to this.

The method was studied and used for the first time in a systematic manner by Pouillet; he employed an iron-platinum couple which he compared with the air-thermometer previously described (page 66). In order to protect the platinum from the action of the furnace-gases, he enclosed it in an iron gun-barrel which constituted the second metal of the junction. Pouillet does not seem to have made applications of this method, which must have given him very discordant results.

Edm. Becquerel resumed the study of his father's couple (platinum-palladium). He was the first to remark the great importance of using in these measurements a galvanometer of high resistance. It is the electromotive force which is a function of the temperature, and it is the current strength that is measured. Ohm's law gives

$$E = RI.$$

In order to have proportionality between these quantities, it is necessary that the resistance of the circuit be invariable. That of the couple necessarily changes when it is heated; this change must be then negligible in comparison with the total resistance of the circuit.

Edm. Becquerel studied the platinum-palladium couple and made use of it as intermediary in all his measurements on fusing-points, but he did not use it, properly speaking, as a pyrometer; he compared it, at the instant of observation, with an air-thermometer heated to a temperature near to that which he wished to measure. He also tried to make a complete graduation of this couple, but this attempt was not successful; he did not take into account the irregularities due to the use of palladium; besides, he made use successively for this graduation of a mercury-thermometer and of an air-thermometer which did not agree with each other. He was led to assume for the relation between the temperature and the electromotive force a very complex expression; the formulæ which he gives contain together twelve parameters, while with the parabolic formula of Tait and Avénarius two suffice; thus

$$e = a + b(t - t_0) + c(t^2 - t_0^2),$$

which well represents the phenomenon for the couple in question up to 1500° .

Regnault took up the study of Pouillet's couple, and he observed such irregularities that he condemned unreservedly the thermoelectric method. But these experiments are hardly conclusive, for he does not seem to have considered the necessity of using a high-resistance galvanometer.

Experiments of Le Chatelier.—The thermoelectric method possesses nevertheless very considerable practical advantages for use in the laboratory as well as industrially, such as:

Smallness of thermoelectric substance;

Rapidity of indications;

Possibility of placing at any distance the measuring apparatus.

Also Le Chatelier decided to take up the study of this method, intending at the outset not to make disappear the irregularities which seemed inherent to the phenomena in question, but to study the law of these irregularities, so as to determine corrections which would permit of making use of this method, at least industrially, for approximate measurements. These investigations showed in their turn that the sources of error observed could be suppressed; the principal one, and the only serious one, came from lack of homogeneity of the metals up to that time employed.

Iron, nickel, palladium, and their alloys are absolutely unsuited for the measurement of high temperatures, because, heated in certain of their points, they give birth to parasite currents, sometimes relatively intense.

Heterogeneity of Wires.—Here, for example, are the electromotive forces observed in carrying a Bunsen flame along beneath a wire of ferronickel of 1 mm. diameter and 50 cm. long; the electromotive forces are expressed in microvolts (millionths of a volt):

Distance...	0.05	0.10	0.15	0.20	0.30	0.35	0.40	0.50
E.M.F. . .	-200	+250	-150	-1000	-500	-200	-50	-200

An electromotive force of 1000 microvolts is that given by the usual couples that we are going to study for a heating of 100°. With such anomalies as above there could hardly be any measurements possible.

These anomalies may sometimes be due to accidental variations in the composition of the wires, but in general there is no pre-existing heterogeneity; a physical heterogeneity due to the heating is produced. Iron and nickel, heated respectively to 750° and 380°, undergo an allotropic transformation, incompletely reversible by rapid cooling.

In the case of palladium there are produced, besides, phenomena of hydrogenation which change completely the nature of the metal, so that a metal initially homogeneous may become by simple heating quite heterogeneous and form a couple.

Certain metals and alloys are quite free from these faults, notably platinum and its alloys with iridium and rhodium. The irregularities previously observed are thus due to the employment of iron and palladium in all the couples tried.

A second source of error, less important, comes from the annealing. In heating a wire at the dividing-point between the hardened part and the annealed part there is developed a current whose strength varies with the kind of wire and the degree of hardness. The twisting that a wire has undergone at a point suffices to produce a hardening. A couple whose wires are hard drawn throughout a certain length will give different indications according to the point of the wire where the heating ceases. Here are results in microvolts obtained with a platinum 1 platinum-iridium

(20 per cent I_2) couple (platinum-iridium alloy is very easily annealed):

	100°	445°
Before annealing.....	1100	7200
After annealing.....	1300	7800
	200	600
Difference.....		

We shall study successively:

1. The choice of the couple;
2. The choice of methods of measurements;
3. The sources of error;
4. The standardization.

Choice of the Couple.—Account must be taken of the electromotive force, the absence of parasite currents, the inalterability of the metals used.

a. Electromotive Force.—This varies enormously from one couple to another. Below are several such electromotive forces given between 0° and 100° by metals that can be drawn into wires and opposed to pure platinum.

	Microvolts.
Iron.....	2100
Hard steel.....	1800
Silver.....	900
Cu + 10% Al.....	700
Gold.....	600
Pt + 10% Rh }	500
Pt + 10% Ir }	500
Cu + Ag.....	500
Ferronickel.....	100
Nickel-steel (5% Ni).....	0
Manganese steel (13% Mn).....	- 300
Cu + 20% Ni.....	- 600
Cu + Fe + Ni.....	- 1200
German silver (15% Ni).....	- 1200
“ “ (25% Ni).....	- 2200
Nickel.....	- 2200
Nickel-steel (35% Ni).....	- 2700
“ “ (75% Ni).....	- 3700

Barus * studied certain alloys between 0° and 930°; he obtained the following results:

	Microvolts
Iridium (2%)	791
" (5%)	2830
" (10%)	5700
" (15%)	7900
" (20%)	9300
Palladium (3%)	982
" (10%)	9300
Nickel (2%)	3744
" (5%)	7121

Here is another series made at the boiling-point of sulphur with alloys of platinum containing 2, 5, and 10 per cent of another metal:

Metals.	Au	Ag	Pd	Ir	Cu
2%	— 242	— 18	+ 711	+1384	+410
5	— 832	— 105	+ 869	+2035	+392
10	—1225	—158	+1127	+3228	+257
	Ni	Co	Fe	Cr	Sn
2%	+2166	+ 26	+3020	+2239	+261
5	+3990	—170	+3313	+3123	+199
10	+5095	— 41	+3962	+3583	+151
	Al	Mn	Mo	Pb	Sb
2%	+779	+ 758	+ 263	—268	+1155
5	+938	+2206	+1673	+338	
10	+ 766		

* Barus, at the same time as Le Chatelier, studied the thermoelectric measurement of high temperatures; he sought to determine the temperatures of formation of the rocks of the earth's crust and also to determine the advantages and limitations of the various pyrometric methods; his very considerable investigations are little known. There is a great mass of numerical data in his work, use of which will be made here.

Of all these metals, the only ones to keep by reason of their high electromotive force are the alloys of platinum with iron, nickel, chromium, iridium, and rhodium. The following table gives, in microvolts, the electromotive forces of the 10 per cent alloys of these five metals up to the temperature of 1500°:

Temperatures.	Fe	Ni	Cr	Ir	Rh
100°	438	646	405	517	565
448	3962	4095	3583	3228	3450
930	9200	9100	11000	8500
1500	19900	20200	15100

b. Absence of Parasite Currents.—The alloy with nickel gives parasite currents of great intensity, as do all the alloys of this metal. It would be probably the same with iron, but there are no data on the matter. Chromium does not seem to present the same inconvenience: it forms an alloy difficult to fuse and, for this reason, difficult to prepare. With the alloys of iridium and of rhodium there is no production of parasite currents.

There remain, then, but three metals to consider: iridium, rhodium, and chromium. Of the alloys of these metals with platinum, that of iridium is the one which hardens the most easily.

c. Chemical Changes.—All the alloys of platinum are slightly alterable. Those of nickel and of iron, at high temperatures, assume a slight superficial brownish tint caused by oxidation of the metal. No test has been made to see if, after a long time, this attack would reach even to the interior of the wires.

The alloys of platinum, and platinum itself, become brittle by simply heating them long enough, especially

between 1000° and 1200°; this is due without doubt to crystallization. The platinum-iridium alloy undergoes this change much more rapidly than the platinum-rhodium, and this latter more rapidly than pure platinum.

But a much more grave cause of the alteration of platinum and its alloys is the heating to high temperatures in a *reducing atmosphere*.

All the volatile metals attack platinum very rapidly, and a great number of metals are volatile. Copper, zinc, silver, antimony, at their points of fusion, already emit a sufficient quantity of vapor to alter rapidly the platinum wires placed in the neighborhood. These metallic vapors, that of silver excepted, can only exist in a reducing atmosphere. Among the metalloids, the vapors of phosphorus and of certain compounds of silicon are particularly dangerous. It is true that one is rarely concerned with these uncombined true metalloids, but their oxides in the presence of a reducing atmosphere are more or less completely reduced. In the case of phosphorus it is not only necessary to shun phosphoric acid, but also acid phosphates of all the metals and the basic phosphates of the reducible oxides; thus silicon, silica and almost all the silicates, clay included, must be avoided.

The reducing flames in a fire-clay furnace lead little by little to the destruction of the platinum wires. It is thus indispensable to protect the couples against any reducing atmosphere by methods which will be indicated further on.

In taking account of these different considerations, electromotive force, homogeneity, hardness, alterability by fire, we are led to give the preference to the couple Pt—Pt+10% Rh, with the possibility of replacing the rhodium by iridium and perhaps by chromium. In the case of iridium it is necessary to recall that the preliminary annealing of the wires is very important, and that pro-

longed heating near 1100° , even in an oxidizing atmosphere, is dangerous for the couple.

Methods of Electric Measurements.—Two methods may be used to measure the electromotive force of a couple: the method of opposition and the galvanometric method. From the scientific point of view, the first alone is rigorous; it is sometimes made use of in laboratories. The second method is simpler, but possesses the inconvenience of giving only indirectly the measure of the electromotive force by means of a measurement of current strength. This inconvenience is more apparent than real in the later forms of instrument, as will be shown.

Method of Opposition.—A complete installation consists of:

1. A *standard cell*, which should not have any current pass through it, and serves to determine, as term of comparison, a difference of potential between two points of a circuit through which there is a current given by an accumulator. The cell used may be a Latimer-Clark, whose electromotive force for small changes in temperature is

$$e = 1.434 \text{ volts} - 0.00080(t^{\circ} - 15').$$

This cell is made up as follows: zinc, sulphate of zinc, mercurous sulphate, mercury. The zinc sulphate should be perfectly neutral; for that the saturated solution of the salt is heated to 40° or more with an excess of zinc oxide to saturate the free acid, is then treated with mercurous sulphate to remove the excess of zinc oxide dissolved in the sulphate, and finally crystallization is produced at 0° ; one thus obtains crystals of zinc sulphate which can be immediately used.

This element is very constant. With a surface of zinc electrode equal to 100 sq. cm. and a resistance of 1000

ohms, the dropping off of the electromotive force of the cell in action does not reach $\frac{1}{1000}$; with 100 ohms only, this would be $\frac{1}{200}$. Practically it is possible, with a resistance of 1000 ohms, to limit the surface of the electrodes to 30 sq. cm., and to do away with the use of accumulators. But then the theoretical advantage of the absolute rigor of the method employed is lost.

There are other forms of standard cell which possess the advantages of portability and small temperature coefficient rendering them better adapted for ordinary use than the original Clark form. The Carhart-Clark cell is made with unsaturated mercurous sulphate and has the E.M.F.

$$e = 1.440 - 0.00056(t^\circ - 15^\circ).$$

In the Weston cadmium cell, cadmium and cadmium-sulphate replace the zinc and zinc-sulphate of the Clark cell, and in the portable form of the cell the cadmium-sulphate is unsaturated. This cell has no temperature coefficient so that no precautions as to temperature control have to be taken. This cell also recovers rapidly after maltreatment. Its E.M.F. is 1.0198 volts.

The values of the E.M.F.s given above are in international volts which are legal in the United States and used by the National Bureau of Standards. The Reichs-anstalt have found the E.M.F. of the Clark cell to be 1.433, and use this value.

2. A *resistance-box* which includes a fixed resistance of about 1000 ohms and a series of resistances of 0 to 10 ohms, permitting by their combinations to realize in this interval resistances varying by tenths of an ohm. One may, for greater simplicity, but by sacrificing precision, replace this series of small resistances by a single Pouillet's rheostat having a total resistance of 10 ohms. This appa-

ratus consists of two parallel wires of a meter in length and 3 mm. in diameter, made of an alloy of platinum and 3% copper.

3. A sensitive galvanometer giving an appreciable deflection for 10 microvolts. It is placed in the circuit of the couple. Use may be made here of a galvanometer Deprez-d'Arsonval of small resistance, since this is a case of reduction to zero.

Principle of the Method.—In order to make an experiment, one places by trial the two extremities of the couple in contact with two points of the circuit of the cell chosen so that the couple is not traversed by any current.

In these conditions the electromotive force of the couple is equal and of opposite sign to the difference of potential between the two points of the circuit, and this, in calling

E the electromotive force of the cell,

R the total resistance of the circuit,

r the resistance between the two points considered, has for value

$$e = E \cdot \frac{r}{R}.$$

A modification of this method eliminating the standard cell in actual work with the couple has its advantages. A storage cell at W (Fig. 24) is in series with a rheostat R and a series of coils or combinations of coils and bridge wire represented by AB . The E.M.F. of the standard cell at E is balanced against that of the battery W by varying R , the points of contact M and M' being at A and B and the balance indicated by no current in the galvanometer. The standard cell is now replaced at E by the couple whose E.M.F. is to be measured; M and M' are then varied in position until a balance is again obtained; then

$$e = E \cdot \frac{MM'}{AB}.$$

This is the simplest form of potentiometer.

Use of a Potentiometer.—For exact measurements the resistance-box, mentioned above, may be replaced to great advantage by some form of potentiometer, of which

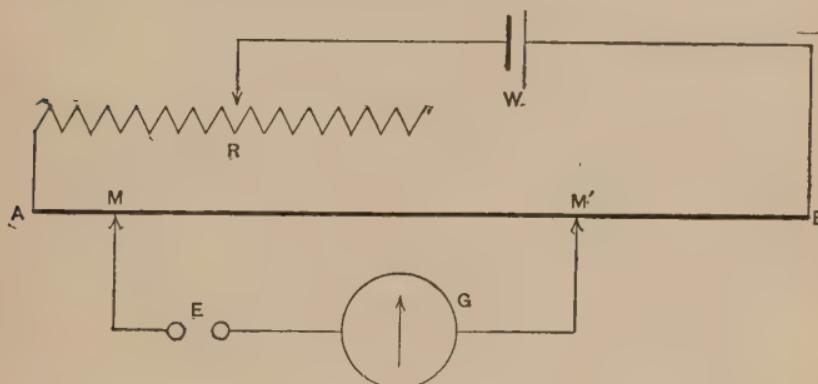


FIG. 24.

there are several on the market, suitable for the determination of small electromotive forces and whose principles we have just described. This type of instrument is illustrated in Fig. 23, p. 117, and has the great convenience of being direct reading, giving the electromotive force directly in decimals of a volt, so that the E.M.F. of a couple at any temperature is determined in a few seconds to an accuracy of one microvolt with a sensitive galvanometer.

The method of taking a measurement is as follows: The dials being set in any position whatever, the standard cell, which is in series with all the coils in the box, is balanced against the battery by varying the rheostat; the switch is then thrown to the E.M.F. side which throws out the standard cell, and the E.M.F. of the couple, attached through leads and a reversing switch to the binding

posts marked E.M.F., is measured by turning the dials until a balance is reached.

For thermoelectric work it is not necessary to have an extremely high resistance potentiometer, 1000 ohms sufficing, but the lower this resistance the greater the care required in the construction and use to avoid uncertain electrical contacts. In practice also the direction of the E.M.F.s should be reversed for every reading to eliminate thermo-E.M.F.s. A sensitive galvanometer is necessary for precise work.

Compensation Method.—This is a modification of the preceding eliminating the use of a potentiometer or carefully calibrated resistance-box, but requiring a calibrated milliammeter and one or more well-known resistances. This method was first used by Holman in thermoelectric work and Fig. 25 illustrates the principle. M is a milliam-

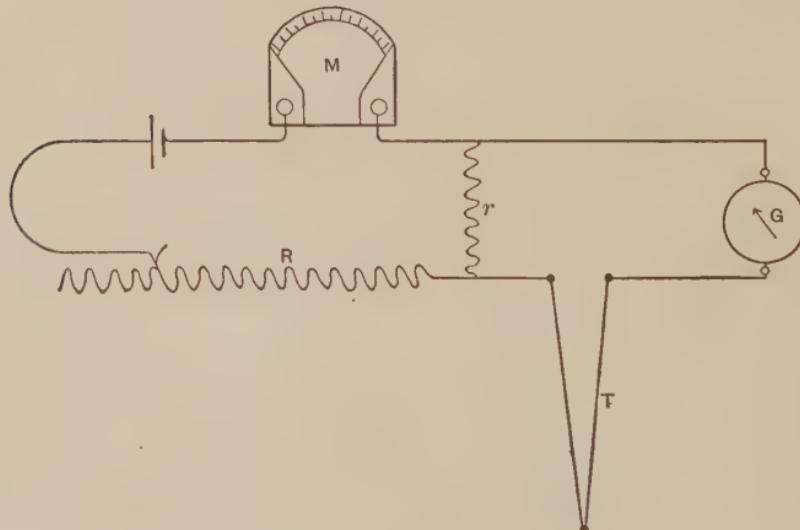


FIG. 25.

meter and r a small (0.1ω) known resistance, R a rheostat with fine adjustment, G the galvanometer, and T the thermo-

couple. The deflection of G is brought to zero by varying R when the product of the current given by M and the resistance r gives the desired E.M.F. With a series of coils to substitute at r , the range of measurable temperature may be indefinitely extended.

Siemens and Halske sell a convenient form of this apparatus as devised by Lindeck of the Reichsanstalt.

Various other special forms of apparatus for the exact measurement of thermocouple E.M.F.s have been devised, but they are all modifications, more or less complicated, of the above.

Galvanometric Method.—The measurement of an electromotive force may be reduced to that of a current; it suffices for that to put the couple in a circuit of known resistance, and from Ohm's law we have

$$E = \frac{I}{R}.$$

If the resistance is not known, but is constant, the electromotive force will be proportional to the current strength, and that will suffice, on the condition that the graduation of the couple is made with the same resistance. If this resistance is only approximately constant, the relation of proportionality will be only approximately exact.

This method is the one used in practically all industrial practice, and to-day galvanometers can be had satisfying all the requirements of which we shall treat in the following paragraphs. In many quarters the thermoelectric pyrometer has been discredited because instruments giving evidently unreliable results were used. With a better understanding of the requirements and the meeting of them by manufacturers this prejudice is disappearing.

Resistance of Couples.—The wires of the couple make

necessarily a part of the circuit in which the current strength is measured, and their resistance varies with increase of temperature. It is important to take account of the order of magnitude of this inevitable change of resistance.

Barus has made a systematic series of observations on the alloys of platinum with 10 per cent of other metal. The relation between the resistance and the temperature being of the form

$$R_t = R_0(1 + \alpha t),$$

he obtained the following results:

	Pt (pure)	Au	Ag	Pd	Ir	Cu	Ni	Fe	Cr	Sn
Specific resistance in microhms (R)	15.3	25.6	34.8	23.9	24.4	63.9	33.7	64.6	42	39
1000α	2.2	1	0.7	1.2	1.2	0.2	0.9	0.4	0.5	0.7

Other tests gave the figures below:

	5% Al	5% Mn	10% Mo	5% Pb	2% Sb	5% Bi	2% Zn	5% Zn
R_0	22	50	17.6	7.7	29.5	16.6	47.8	25
1000α	1.5	0.4	1.9	1.8	1	2	0.3	1.1

The coefficient α is taken between 0° and 357° (boiling-point of mercury).

The experiments of Le Chatelier, for the couples that he used, gave the following results:

For platinum

$$R = 11.2(1 + 0.002t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

For rhodium-platinum (10% Rh)

$$R = 27(1 + 0.0013t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

Holborn and Wien found for pure platinum

$$R = 7.9(1 + 0.0031t) \text{ between } 0^\circ \text{ and } 100^\circ,$$

$$R = 7.9(1 + 0.0028t) \text{ between } 0^\circ \text{ and } 1000^\circ.$$

In the greater number of cases use is made of couples 1 m. in length, whose wires are 0.5 mm. in diameter; their resistance, which is about 2 ohms cold, is doubled at 1000°. If use is made then of a galvanometer of a resistance of 200 ohms and if the variation of the resistance of the couple is neglected, the error is equal to $\frac{1}{100}$. In general this error is still less except in certain industrial uses. Thus in the laboratory the length heated rarely exceeds 10 cm., and then the error reduces to $\frac{1}{1000}$.

Galvanometers. — The earliest measurements, those of Becquerel and of Pouillet, were made with needle-galvanometers controlled by terrestrial magnetism. These apparatus, sensible to jarring, require delicate adjustment, and the readings take a long time. The use of these instruments would have prevented the method from becoming practical. It is only thanks to the use of movable-coil galvanometers of the Deprez-d' Arsonval type that the thermo electric pyrometer has been able to become, as it is to-day, an apparatus in current usage.

This apparatus (Fig. 26) is composed of a large horseshoe magnet between whose poles is suspended a movable frame through which the current passes. The metallic wires, which serve at the same time to suspend the coil and bring in the current, undergo then a torsion which is opposed to the displacement of the coil.

The latter stops in a position of equilibrium which

depends both on the strength of the current and the value of the torsion couple of the wires. To these two forces is added, in general, a third, due to the weight of the coil, which causes disturbing effects often very troublesome. We shall speak of this further on.

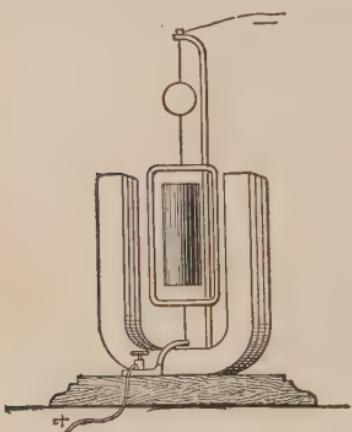


FIG. 26.

stretched before a small opening conveniently lighted.

These movable-coil galvanometers were for a long time considered by physicists as unsuited for any quantitative measurements; they were only employed in null methods and made accordingly. In order to render them suitable for quantitative measurements of current it was necessary to attend to a series of details of construction, previously neglected. Here are the most important among these.

1. The *movable coil* should possess a resistance as little variable as possible with the surrounding temperature in order to avoid corrections always very uncertain. The coils of copper wire ordinarily used to augment the sensitivity should be absolutely discarded; use should be made of coils of German silver or of similar metal with small temperature coefficient such as manganin.

2. The spaces which separate the coils, from the poles of the magnet, on the one hand, and from the central soft-iron core on the other, should be sufficiently great to avoid with certainty any accidental friction which would prevent the free movement of the coil. A width of

2 mm. is convenient; it will hardly do to decrease this. The rubbings to look out for do not come from the direct contact of the frame with the magnet: these latter are too visible to escape unseen. Those which are to be guarded against come from the rubbing of filaments of silk which stand out from insulating covering of the metallic wires, and from the ferruginous dust which clings to the magnet. It is here, it would seem, that the most serious source of error is met with in the use of the movable-coil galvanometer as measuring instrument. There is no warning indication of these slight rubbings which limit the displacement of the coil without, however, taking from it its apparent mobility.

3. The suspending wire should be as strong as may be to support the coil without being exposed to breaking by shocks; on the other hand, it should be very fine, so as not to have too great a torsion couple. Two different artifices help to reconcile somewhat these two opposed conditions: the use of the mode of suspension of Ayrton and Perry, which consists in replacing the straight wire by a spiral made of a flattened wire, or more simply the use of a straight wire flattened by a passage between rollers.

The first method offers the greatest security from shocks; it is, on the other hand, more difficultly realizable; minute precautions should be taken to prevent any rubbing between adjoining spirals. The second method allows more easily having the large angular displacements which are indispensable when it is desired to take readings upon a dial.

The most essential property necessary for the wires is absence of permanent torsion during the operations. These torsions cause changes of zero which may render worthless all the observations if account is not taken of this, which complicates matters considerably if such cor-

rection has to be made. This result is reached by using wires as long as possible, having not less than 100 mm. length, and by avoiding giving to them an initial torsion, a precaution that should be kept constantly in mind, which it often is not. When one wishes to adjust the coil to the zero of graduation, one turns often haphazard either one of the wires; it may be then that each of the wires is given an initial torsion of considerable magnitude and of opposite sign. If the two wires are not symmetrical, as is ordinarily the case, the permanent deformation resulting from this exaggerated torsion will cause a continual displacement of the zero which may last for weeks and months, increasing or decreasing during the observations according to the direction of displacement of the coil. This torsion is easy to obviate at the time of construction, but it is not possible to verify later its absence in the case of round wires or spirals except by dismounting the apparatus. On the contrary, by the use of stretched flat wires it is very easy upon simple examination to determine the existence or absence of torsion. This is another reason for employing them.

Finally, use must be made of wires having a very high elastic limit. For that it is necessary that the metal has been hardened, and besides that the metal does not undergo spontaneous hardening at ordinary temperatures. Silver, generally employed as suspension wire, is worthless. A metal, as iron, which even after annealing possesses a high elastic limit, would be perfect if it were not for its too great alterability. One cannot be sure of having uniform hardening, because the soldering of wires, indispensable to assure good contacts, anneals them throughout a certain length. German silver is the metal the most frequently used in galvanometer suspensions destined for pyrometric measurements. The alloy of platinum with 10 per

cent of nickel seems preferable; after annealing it has a high elastic limit, and possesses a tenacity much higher than that of German silver. Its disadvantage is to possess a limit of elasticity twice as great, which reduces by one-half the deflections of a given cross-section of wire. Phosphor-bronze also gives good results.

4. *Installation of the apparatus* for the galvanometers, in which the coil is carried by two opposed *stretched* wires, necessitates special precautions.

In the first place it should be located beyond the influence of jarrings of the ground, which render reading impossible; then it is necessary that its position remain *rigorously* fixed. If, in fact, the two extreme points of suspension of the wires are not exactly in the same vertical, and if the centre of gravity of the coil is not exactly in the line of the two points of suspension, two conditions which can be never rigorously realized, the apparatus constitutes a bifilar pendulum of great sensibility. The slightest jarring suffices to provoke very considerable angular displacements of the coil. To avoid them, the apparatus should rest upon a metallic support attached to a wall of masonry. When the apparatus is placed, as is often the case, upon a wooden table resting upon an ordinary wooden floor, in order to obtain a deflection of the coil, and in consequence a displacement of the zero, it suffices to walk around the table, which causes the floor to bend slightly, or to provoke a current of air, which, in changing the hygrometric state of the legs of the table, causes it to tip somewhat.

Coils freely suspended from above have not these disadvantages.

Different Types of Galvanometer.—A series of galvanometers have been studied especially in view of pyrometric measurements; we shall pass them rapidly in review.

For laboratory researches the usual swinging-coil galvanometer as made by Carpentier is often used. One must make sure that these instruments satisfy well the indispensable conditions which we have mentioned, which is not always the case when these instruments have been constructed with reference to the ordinary experiments of physics. These conditions are:

Coil of German-silver or low-temperature-coefficient wire of a resistance of at least 200 ohms; 400 ohms is better.

Sufficient free space between coil and magnet.

Invariability of zero, even after a considerable deflection of coil.

Installation on a firm support and levelling device.

This laboratory apparatus, the only one which existed at the time of the first investigations of Le Chatelier, was not transportable, and could not be arranged for experiments in industrial works. It was then necessary to devise a special model of galvanometer easy to carry about and to put in place. The apparatus (Fig. 27) is composed of two parts, the galvanometer and the transparent scale with its light. The two parts are symmetrical and, for transportation, may be fixed back to back on the same plank carrying a handle. For observations they are fastened to a wall by means of two nails driven in at a suitable distance apart. The suspension wires, in case of breakage, may be immediately replaced. They carry, soldered to their two ends, small nickel spheres, which one has only to slip on to forked pieces attached to the top and bottom of the coil, and to the supports of the apparatus, respectively. The mirror consists of a plano-convex lens, silvered on the plane face, which gives much sharper and brighter images than the ordinary small mirrors with parallel faces.

Lately, Carpentier has made for the same purpose a galvanometer in which the readings are taken by means of a microscope. It is an easily transportable apparatus and very convenient. It has only the fault to be subject to a displacement of the zero resulting from the unsymmetrical heating of the body of the microscope by the small lamp

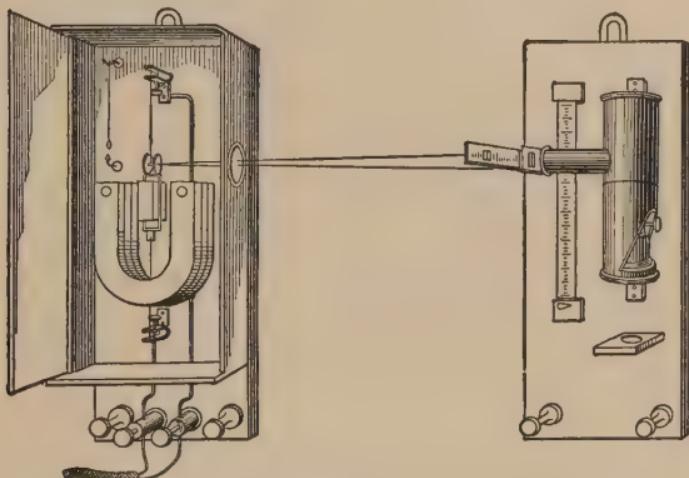


FIG. 27.

which lights the reticule. The stretched wires are replaced by large spirals which offer an absolute resistance to rupture by shock during transportation.

The use of this apparatus necessitates an arrangement which permits, during the observations, putting the galvanometer on open circuit so as to verify the zero reading.

In the three preceding galvanometers the measurement of the deflection of the coil is made by optical means; in the three following, the measurement is made by means of a needle swinging over a scale.

After a study made by Holborn and Wien at the Physikalische Reichsanstalt in Berlin of the Le Chatelier

thermoelectric pyrometer, the firm of Kayser and Schmidt devised a needle-galvanometer (Fig. 28) which works fairly well, although the early forms of this instrument were of too low resistance for many industrial purposes. It has the disadvantage of being somewhat fragile. The suspending wire of the coil does not seem to have more than $1/20$ mm. diameter; the mounting of the apparatus is quite complicated. Repairs cannot readily be made either in the laboratory or works.

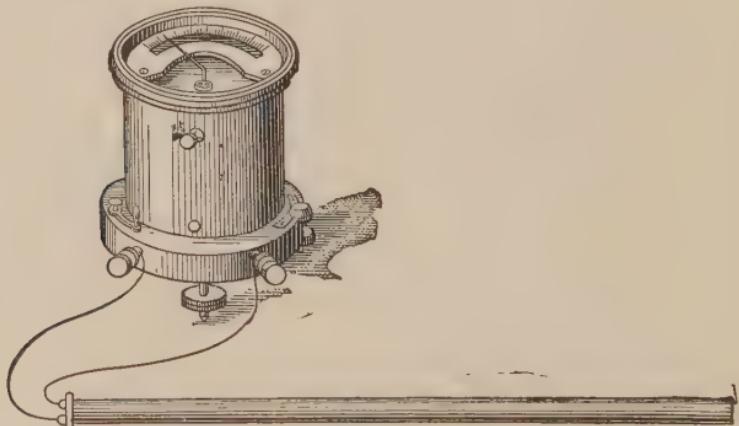


FIG. 28.

The firm Siemens and Halske, which has commenced recently to build Deprez-d'Arsonval galvanometers, has also devised a model of needle-galvanometer suitable for temperature measurements (Fig. 29). Its resistance is 340 ohms, or 400 ohms in the later forms; the scale has 180 divisions, each corresponding to 10 microvolts. There is also a second graduation which gives the temperature directly with the couple sold with the apparatus. Commutators allow of putting the apparatus successively in communication with different thermoelectric couples, if it is desired to take simultaneously several sets of observations.

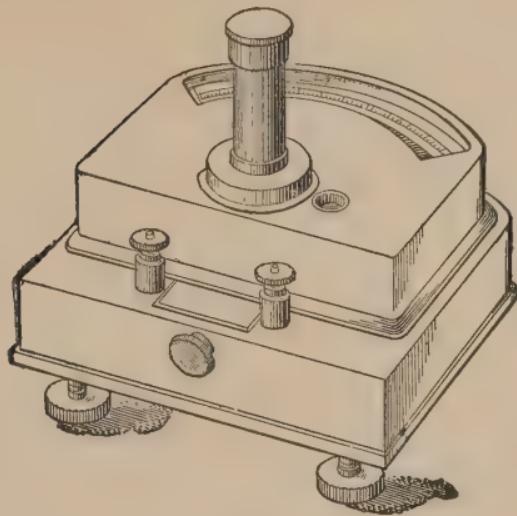


FIG. 29.

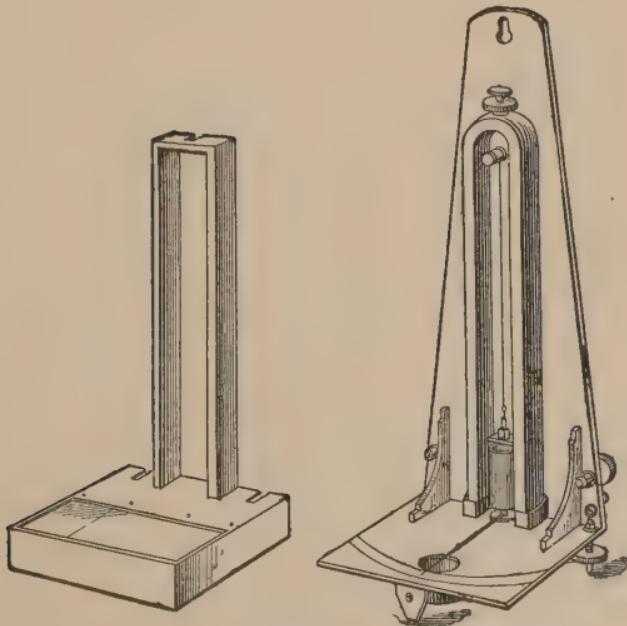


FIG. 30.

Pellin, of Paris, has made, from designs of Le Chatelier, a needle-galvanometer (Fig. 30) of simple construction which can be repaired where it stands. The very long suspension wire is of 10 per cent nickel-platinum; it has $\frac{1}{10}$ mm. diameter and is drawn out flat.

The lower wire is made of a spiral of the same wire of $\frac{1}{20}$ mm. diameter, which is situated in the interior of the iron core so as to insure uniformity of temperature. When the spirals of the suspension are unequally heated by radiation from the room or for other reason, there results considerable displacement of the zero. A spirit-level permits of rendering the apparatus vertical, but it is prudent, by reason of the length of the suspension wire, to make sure directly of the absence of rubbing on the coil. For this a slight jar is given to the apparatus; the point of the needle should take up and keep for a long time a slow oscillatory movement in the direction of its length; the transverse oscillations ceasing rapidly indicate friction upon the coil. Evidently use may be made of a great number of other models of galvanometer which are to be found on the market; but it is necessary to make sure in the first place that they satisfy the conditions necessary for good temperature measurement, which is rarely the case.

Requirements of Industrial Practice.—In many industrial operations it is desirable to know a temperature in the range 400° C. to 1500° C. to 10 degrees. This accuracy can be obtained with industrial forms of the thermo-electric pyrometer, but only when certain conditions are fulfilled by the maker and by the user.

The instrument, sufficiently sensitive and at the same time robust, should have an open scale carefully calibrated; the resistance of the galvanometer should be 400 ohms at least, for use with ordinary platinum-metal

thermocouples, so that varying depths of immersion and changes of resistance of the couple wires with temperature will not appreciably affect the galvanometer readings; the temperature coefficient of the instrument should be negligible and there should be no secondary thermal sources of electromotive force present; the constancy of the zero should be within the desired limit of precision even with continued deflections at the higher points of the scale; a levelling device should be provided and the effect of non-levelling on the readings of the instrument should be small. This last is perhaps the hardest requirement to fulfil, and it is necessary for the user to carefully level any industrial instrument and verify its zero reading before any measurements are taken. If the wires of the couple are attached directly to the galvanometer, as is usually the case, care must be taken that the temperature of the binding-posts remains constant, for if they are heated or cooled they also become sources of E.M.F. and so change the readings of the galvanometer, and in general if anywhere in the circuit there are dissimilar metals joined together there will be parasite currents developed at these junctions for changes of temperature. The user should know at what temperature the scale of his instrument is correct and should be enabled to correct for changes in temperature of the "cold" junctions.

If, for example, the scale of the galvanometer is correct when the cold junctions are at 0° C., the indicated temperature given by the galvanometer should be increased by $\frac{t^{\circ}}{2}$, where t° is the actual temperature of the cold junctions, t° being less than 30° C.

If a new couple is substituted, the E.M.F. scale of the galvanometer will still be correct, but unless the new

couple is identical with the old, the temperature scale will no longer hold.

Arrangement of the Wires of the Couple.—For good working of the couple there are certain practical precautions to be taken, which we shall consider.

Junction of the Wires.—The contacts of the different parts of the circuit should be assured in a positive manner; the best way is to *solder* them. Binding-screws often work loose in time, or the metallic surfaces in contact become oxidized. The importance of this precaution varies with the conditions of the experiments; one can dispense with it for experiments that last only a few hours, because there is little chance that the contacts become modified in so short a time; soldering is on the contrary indispensable in an industrial installation which will have to be used for months without being tested anew.

But in any case the soldering together of the two leads of the couple is absolutely indispensable. It is quite true that the electromotive force is independent of the manner of making contact. The two wires twisted together or soldered will give at the same temperature the same electromotive force. But under the action of heat the twisted parts are soon loosened, and there result bad contacts which increase the resistance of the whole circuit. In general this accident is not noticed until the untying is almost complete, so that one may make before this a whole series of false measurements without being warned.

The best method of soldering is the autogène junction by direct fusion of the wires of the couple; it is necessary, in order to effect this, to have oxygen at hand. One commences by twisting the two leads together for a length of about 5 mm., and they are then clamped above an oxy-hydrogen blast-lamp. Oxygen is admitted through the

central tube, and gas through the annular space; the oxygen is allowed to flow in normal quantity, and the gas in feeble quantity, then one opens progressively the gas-cock. At a certain instant one sees the extremities of the wires melt, giving off sparks; the gas is then shut off. If one waits too long, the junction will melt completely and the two wires separate. With a little practice a junction can be made by touching together, in the oxyhydrogen blast, the two wires held in the hand.

In default of oxygen, the wires may be soldered with palladium, which can be melted by means of a blast-lamp furnished with air, taking care to reduce the action of radiation. A hole is cut in a piece of charcoal in which is placed the junction of the two wires twisted together after having wound about it a wire or a small strip of palladium, and the flame of the lamp is then directed upon the junction.

In the cases in which the couple is not to be used above 1000° , and only in these cases, the soldering may be done still more simply by the use of gold; the ordinary Bunsen flame is sufficient to make this junction.

Insulation and Protection of the Couple.—The two leads should be insulated from one another throughout their length. For this, use is made in the laboratory of glass tubes or pipe-stems, or better still of an asbestos thread wound about the two wires, by crossing it each time between the two (Fig. 35) so as to make a double knot in the form of an eight, each of the wires passing through one of the loops of the eight. This is a convenient method of insulation for laboratory use. The two wires with their envelope form a small rod of considerable rigidity which is easily slipped into apparatus. With this arrangement it is impossible to go above 1200° or 1300° , at which temperature asbestos melts.

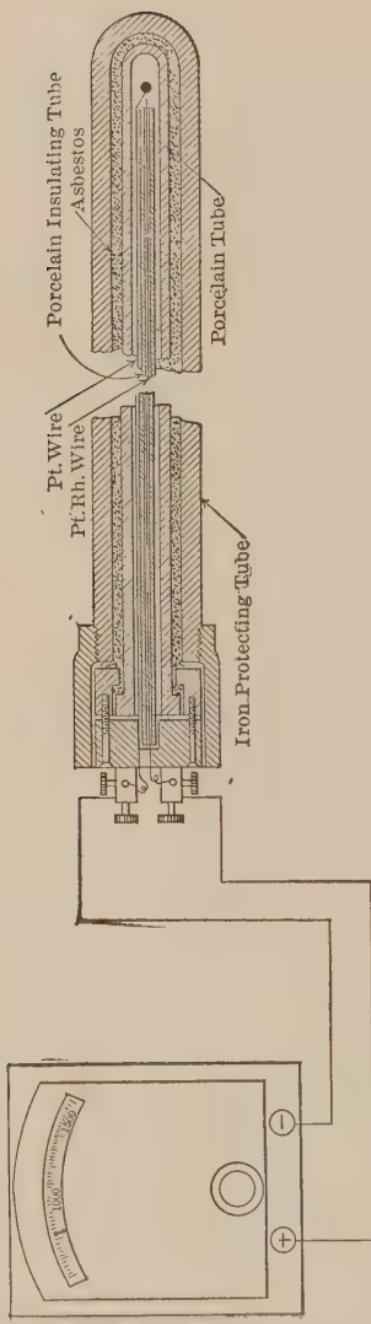


FIG. 31.

For industrial installations it is better to make use of small fire-clay cylinders of 100 mm. in length and 10 mm. in diameter, pierced in the direction of the axis by two holes of 1 mm. diameter, through which pass the wires. One or another of the other forms of insulator is added in sufficient numbers. They are placed, according to the case, in an iron tube or in a porcelain tube. The porcelain tube should be employed in fixed installations in which the temperatures may exceed 800°. One may, as does Parvillée in his porcelain furnaces (Fig. 32), place the porcelain tube in the lining of the furnace in such a way that its end is flush with the inner surface of the lining. An open space of a decimeter cube is cut in the lining about this extremity of the tube. This method makes easier the establishment of temperature

equilibrium without subjecting the tube to too great chances of breaking by accidental blows.

The iron tube is used for temperatures not exceeding 800° , in the lead baths serving to temper steel for example, and for movable couples which are exposed to heat only during the time necessary to take the observations. In this case the junction is placed some 5 cm. beyond the insulators and the iron jacket. The wires take up the temperature within 5 seconds, and the observation can be

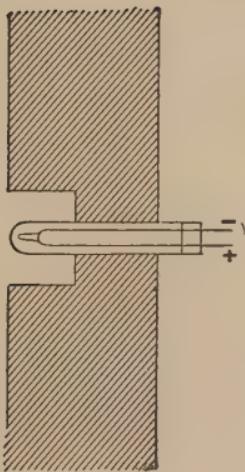


FIG. 32.

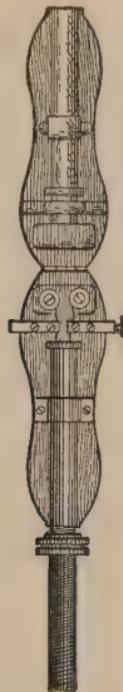


FIG. 33.

taken before the tube becomes hot enough to be burned, even in furnaces for steel whose temperatures exceed 1600° , and before the wires have had time to be altered even in strongly reducing flames. The other extremity of the iron tube carries a wooden handle (Fig. 33) where

are located, outside, the binding-posts for the galvanometer leads, and inside an extra length of wire for the couple to replace portions burned or broken off. The above design gives the arrangement of this handle.

In all cases in which the furnace whose temperature it is desired to measure is under a reduced pressure, suitable precautions must be taken to prevent any permanent entrance of cold air by the orifice necessary for the introduction of the tube, as well before as during an observation. Otherwise one runs the chance of having inexact results.

In the case of prolonged observations in a reducing atmosphere or in contact with melted bodies, as the metals capable of altering the platinum, the couple should be protected by enclosing it in a covering impermeable to the melted metals and to vapors. For fixed installations in industrial works use should be made of a porcelain tube, or one of iron, closed at the extremity where the junction is located; in this case the dimensions of the tube are unimportant. For laboratory investigations it is indispensable, on the contrary, to have around the wires a covering of as small diameter as possible. If it is simply a question of protecting the couple against the action of non-volatile metals, the simplest way is to use, as does Roberts-Austen, a paste sold in England under the name of Purimachos, which serves to repair the calettes employed in moulding. We have made an analysis of this which gave the following composition after desiccation at 200°:

Alumina and iron.....	14
Soda.....	3.2
Water.....	2.6
Silica (by difference)	80.2

It is a very finely powdered quartz to which is added 10 per cent of clay, and diluted with a solution of silicate of

sodium. To use it the matter is diluted so as to form a thick paste, and the couple is dipped in it the required length, arranging the wires parallel to each other at a distance apart of about 1 mm.

The whole may then be dried and calcined very rapidly, without fear of snapping the covering, as would happen with clay alone; but this covering is not sufficiently impermeable to protect the couple against the very volatile metals, as zinc. It is better, in this case, to use small porcelain tubes of 5 mm. inside diameter, 1 mm. thickness of wall, and 100 mm. long, straight or curved according to the usage to which they are to be put.

The couple insulated by asbestos thread, or by a small inner porcelain tube of 1 mm. inside diameter, as has been said previously, is pushed down to the bottom of the tube. If one has not at hand such tubes of porcelain, and it is required to make a single observation at a temperature not exceeding 1000° , as, for instance, a standardization in boiling zinc, one may use a glass tube. It melts and sticks to the asbestos, which holds a thick enough layer to itself to protect the platinum. But, on cooling, the tube breaks, and it is necessary to make a new set-up for each operation. This is not practicable for continuous observations.

Cold Junction.—In general, in a thermoelectric element, one distinguishes the hot junction and the cold junction. The latter is supposed kept at a constant temperature. In order to realize rigorously this arrangement, three wires are necessary, two of platinum and one of an alloy connecting two junctions. This theoretical arrangement is practically without interest, and the second junction is always dispensed with. If, in fact, the temperature of the whole circuit exclusive of the hot junction is uniform, the presence or the absence of the cold junction does not affect the electromotive force; if this temperature is not uniform

the second junction is not advantageous, for there is then in the circuit an infinity of other junctions just as important to consider: the junctions of the copper leads with the platinum wires, those of the galvanometer leads and of the different parts of the galvanometer among themselves.

One must satisfy himself as well as may be as to the uniformity of temperature in the cold circuit, and rigorously of the equality of temperature between corresponding junctions, particularly those of the two platinum wires with the copper leads. These uncertainties in the temperature of the cold junctions are an important source of error in the measurement of temperatures by thermoelectric couples, but for ordinary practice they are easily eliminated. In order to realize exact measurements, precise to 1° , for instance, it will be necessary to have completely homogeneous circuits, including the galvanometer, with the single exception of the junctions of the platinum wires with the conducting leads; these should be immersed in the same bath at constant temperature. It would be necessary for this that the constructors of galvanometers limit themselves to the use of the same German silver for all parts of the apparatus, wires of the coil, suspending wires, leads, and parts of the coil. That is difficult to obtain.

In the standardization of thermocouples for exact work it is customary to immerse the cold junctions, *i.e.*, the points of contact of the copper leads and platinum-metal wires, in an oil-bath in ice. With the potentiometer, irregularities due to other sources of E.M.F. in the circuit are eliminated by reversing simultaneously the battery current and the couple circuit.

Graduation.—There exist no two couples possessing exactly the same electromotive force, although Heraeus has made up several kilometers of pure platinum and platinum-rhodium which give practically identical E.M.F.s

when made up into couples. If it were necessary each time to make a comparison with the air-thermometer, this obligation would render illusory the advantages of the thermoelectric method. Practically one is satisfied to make this comparison by means of certain fixed points of fusion and ebullition. But how many must be taken? That depends on the nature of the function connecting the electromotive force and the temperature.

Formulæ.—Avenarius and Tait have shown that up to 300° the electromotive force of a great number of couples was represented in a manner sufficiently exact by means of a parabolic formula of two terms:

$$e = a(t - t_0) + b(t^2 - t_0^2).$$

The experiments of Le Chatelier on the platinum-palladium couple have shown that the same formula holds also for this couple up to the fusing-point of palladium:

$$e = 4.3t + \frac{7.3}{1000}t^2.$$

$t = 100$	445	954	1,060	1,550
$e = 500$	2,950	10,900	12,260	24,030

But this law fails completely for couples made of pure platinum and an alloy of this metal.

Here are three series of determinations made with different couples:

Barus. Pt—Pt 10% Ir.		Le Chatelier. Pt—Pt 10% Rh.		Holborn and Wien. Pt—Pt 10% Rh.	
t	e	t	e	t	e
300	2,800	100	550	100	565
500	5,250	357	2,770	200	1,260
700	7,900	445	3,630	400	3,030
900	10,050	665	6,180	600	4,920
1100	13,800	1060	10,560	800	6,970
		1550	16,100	1000	9,080
		1780	18,200	1200	11,460
				1400	13,860
				1600	16,220

Holman has shown that the results of Holborn and Wien may be expressed by a logarithmic formula containing only two parameters. Le Chatelier showed that his results could also be represented by the Holman formula, and in general it may be said that throughout the range of ordinary use of the thermocouple the logarithmic formula satisfies the results of observations to 2° C., or well within the limits of all except the most accurate work.

Holman's formula is as follows:

$$(1) \quad \sum_0^t e = mt^n,$$

where $\sum_0^t e$ is the electromotive force of the couple for any temperature t when the cold junction is kept at zero centigrade. The two constants are readily computed or evaluated graphically, and the resulting plot serves indefinitely for the determination of any temperature with a given couple. The equation does not apply in the region in which the thermocouple is insensitive, that is, below 250° C. It may be written

$$(2) \quad \log \sum_0^t e = n \log t + \log m;$$

so that if $\log e$ be plotted as abscissas and $\log t$ as ordinates, a straight line is obtained.

The results obtained by Le Chatelier quoted above satisfy the equation

$$\log e = 1.2196 \log t + 0.302;$$

e is expressed in microvolts.

The following table gives a comparison of the results observed with those calculated by means of the preceding formula:

t (observed)	t (comp.)	e (in microvolts)	$\log e$	$\log e - 0.3020$	$\frac{\log t =}{\log e - 0.3020}$ 1.2196
100°	102°.5	565	2.7520	2.4500	2.010
$\Delta =$	(+2.5)				
200	198.2	1,260	3.1004	2.7984	2.927
	(-1.8)				
400	405	3,030	3.4814	3.1794	2.608
	(+5)				
600	602	4,920	3.6920	3.3900	2.780
	(+2)				
800	800	6,970	3.8432	3.5412	2.903
	(0)				
1000	996	9,080	3.9581	3.6561	2.998
	(-4)				
1200	1208	11,460	4.0591	3.7571	3.082
	(+8)				
1400	1410	13,860	4.1418	3.8398	3.150
	(+10)				
1600	1603	16,220	4.2100	3.9080	3.205
	(+3)				

The same formula has been applied successfully to the observations of Barus on platinum-iridium couples.

Holborn and Day in their very elaborate direct comparison of the nitrogen-thermometer with thermocouples made of the various platinum metals find that above 250°, if a precision of 1° is sought, a three-term formula is required to express the relation between E.M.F. and temperature.

The formula

$$\sum_0^t e = -a + bt + ct^2$$

is the one they have used. The labor involved in computation with this form is considerable, and unless a very great accuracy is required Holman's formula is amply sufficient, when the uncertainty of the absolute values of high temperatures is considered.

Stansfield deduces from theoretical considerations the formula

$$T \frac{dE}{dT} = aT + b,$$

which may be written

$$E = aT + b \log T + c,$$

a form which satisfies the experimental results determined with pure platinum wires. This form possesses no practical advantage over that of Holborn and Day, unless it be its usefulness, by employing the graphical method, in detecting slight errors in fusing-points. The values of $\frac{dE}{dT}$ at the points of fusion can be obtained from the T vs.

E plot, and the T vs. $\frac{dE}{dT}$ curve thus constructed throws into prominence the experimental errors at these points. As the above formulæ indicate, the curve for the platinum metals constructed with T as abscissas and $T \cdot \frac{dE}{dT}$ as ordinates is a straight line. The errors of the method are less than 2° at 1000° . The ordinary metals, on the other hand, give nearly a straight line for the curve T vs. $\frac{dE}{dT}$.

Fixed Points.—The Holman formula includes only two parameters which may be determined by means of two observations. It will suffice therefore to have two fixed points to graduate a couple, on the condition, however, that they be taken far enough apart. It will be well to choose them in the neighborhood of the region of temperatures in which the couple is to be especially employed. If two observations are sufficient theoretically, it will be prudent in practice to utilize for the graduation a greater number of fixed points so as to have a check on the accuracy of the observations. The points to be recommended by reason of the accuracy with which they are known, and for their ease of reproduction, are the following:

Ebullition of water;

Ebullition of naphthaline, or the fusion of tin;

Ebullition of sulphur, or the fusion of zinc;

The fusion of gold or copper, or in default the ebullition of zinc;

Fusion of platinum.

The fusing-points are easier to use than the boiling-points at temperatures higher than 500°. The lower boiling-points, water, naphthaline, and sulphur, can be very exactly determined, but the boiling-point of zinc is almost impossible to get well. The fusing-points should be used above 900° C.

For the *boiling-points* of water, naphthaline, and sulphur it is convenient to make use of an arrangement due to Barus (Fig. 34). This consists of a tube of thin glass, similar to test-tubes, of 15 mm. inside diameter, 300 mm. long, with a small bulb at 50 mm. below the open end. It is surrounded with a plaster muff of 150 mm. height and 100 mm. diameter which has been cast about the glass tube inside of a thin metallic cylinder forming the outside surface. The bulb is immediately above the plaster jacket, below which the tube, closed at its lower end, extends to a distance of 70 mm. As soon as the plaster has begun to set, the glass tube is taken out, giving it a slight twisting motion. The cylinder is left to dry, and the tube is again put in place. This allows, when the tube is broken, of taking it out and replacing it, which would be difficult if it adhered to the plaster. A jacketed Victor Meyer tube may also be used.

The lower free portion is heated by a Bunsen flame gently at first, then without any special precaution, once

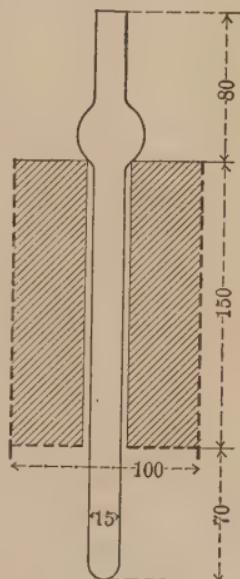


FIG. 34.

boiling sets in. The liquid at rest should occupy two-thirds of the height of the free end of the tube. The heating is continued until the liquid coming from the condensation of the vapor runs abundantly down the walls of the bulb. The flame is then adjusted so that the limit of condensation of the liquid, which is very sharp, remains constantly midway up the bulb. There is then a perfectly uniform temperature in the interior of the glass tube throughout the height of the plaster cylinder. The junction of the couple is inserted and the coil of the galvanometer takes up a fixed invariable position. It is well to prevent the liquid from running down about the couple by placing a small cone of platinum or asbestos above the junction. Electric heating may also be used.

For the boiling-point of zinc Barus made small crucibles of porcelain very ingeniously arranged, but also very complicated, besides being fragile and costly. One can make use more simply of a porcelain crucible 70 mm.

deep (Fig. 35), filled with melted zinc for 50 mm. of its depth, and, above, 20 mm. of charcoal-dust. A cone pierced with a central hole lets pass a small porcelain tube containing the couple. The whole is heated until there is seen a small white flame of zinc escaping from the crucible. It is indispensable that the openings for the escape of zinc vapor be large enough. They tend, indeed, to become clogged by a deposit of zinc oxide which solders at the same time the cover to the crucible, and this causes

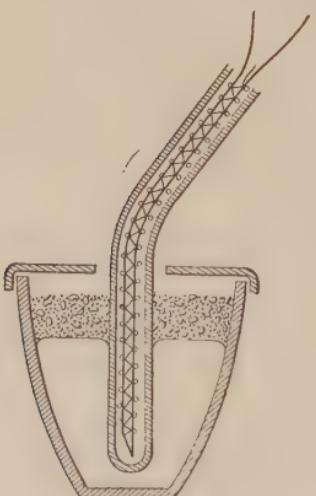


FIG. 35.

an explosion when there is no longer vent for the zinc vapors.

Use may be made to advantage for this heating, and still more for the heating of small crucibles to a very high temperature, of a furnace model of English make (Fig. 36), which has the advantage to resist almost indefinitely the action of heat and to be very easily repaired. The principle of the construction of these furnaces is to make them of two concentric layers. The outer covering of fire-clay, bound together by iron, gives solidity to the furnace; it receives but indirectly the action of the heat, and is not exposed to cracking by shrinkage under the action of too high temperatures. The inner envelope, which alone receives the action of the heat, is made of large-grained quartz sand, grains of 1 mm., mixed with a small amount of a flux. At a high temperature the quartz does not shrink as does clay; it expands, on the contrary, passing over to the form of amorphous silica with a change of density from 2.6 to 2.2. But this transformation is effected only with extreme slowness, otherwise it would burst the furnace. If by chance this inner lining falls down, it is

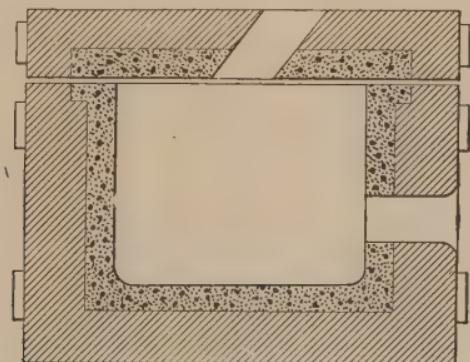


FIG. 36.

easily replaced by putting into the furnace a glass jar of suitable diameter, surrounded with a sheet of oiled paper, and packing about this, coarse quartz sand slightly mois-

tened with a sirupy solution of alkaline silicate. The furnace is heated by means of a lateral opening with a Fletcher lamp, which has the advantage of being sturdy, or with an ordinary blast-lamp.

In the use of *fusing-points* there are several cases to distinguish. If one wishes to employ a considerable quantity of metal, as with zinc, lead, and tin, the easiest way is to melt them in a crucible, into which is thrust the properly protected couple, and let the whole cool. There is observed with no difficulty the stationary temperature of solidification.

If only a small quantity of metal can be employed, as in the case of gold, or if there is no installation for heating the crucibles, it is possible to obtain the fusing-points as follows: One wraps about the junction, so as to cover it completely, a fine wire of the metal chosen (it suffices with a little practice to use but a centigramme of metal), and then places the couple in an enclosure at stationary temperature slightly higher than that of fusion, or at temperature increasing very regularly. The galvanometer readings are noted, which at the instant of fusion show a momentary halt followed by a sudden jump. But this perturbation is the more feeble the smaller the metallic mass, and a certain practice is necessary in this kind of observation in order to seize with certainty the halting-point. It is evident that the heating must be absolutely regular. It is impossible to obtain this result with a free flame, which is always unsteady. In order to have a stationary temperature, use is made in the laboratory of a tube or a muffle placed in a furnace that has been lighted for some time; at industrial works, a chimney or flue for the escape of smoke. In these enclosures the temperature varies from spot to spot, and one can, after a few trials, find the proper temperature. In order to work at increas-

ing temperatures, which is the most convenient in the laboratory, the junction is placed, properly prepared, in a little crucible filled with powdered, non-fusible, poor conducting material, or else the junction is simply wrapped in a bullet of plaster, clay, or Purimachos. Care is taken

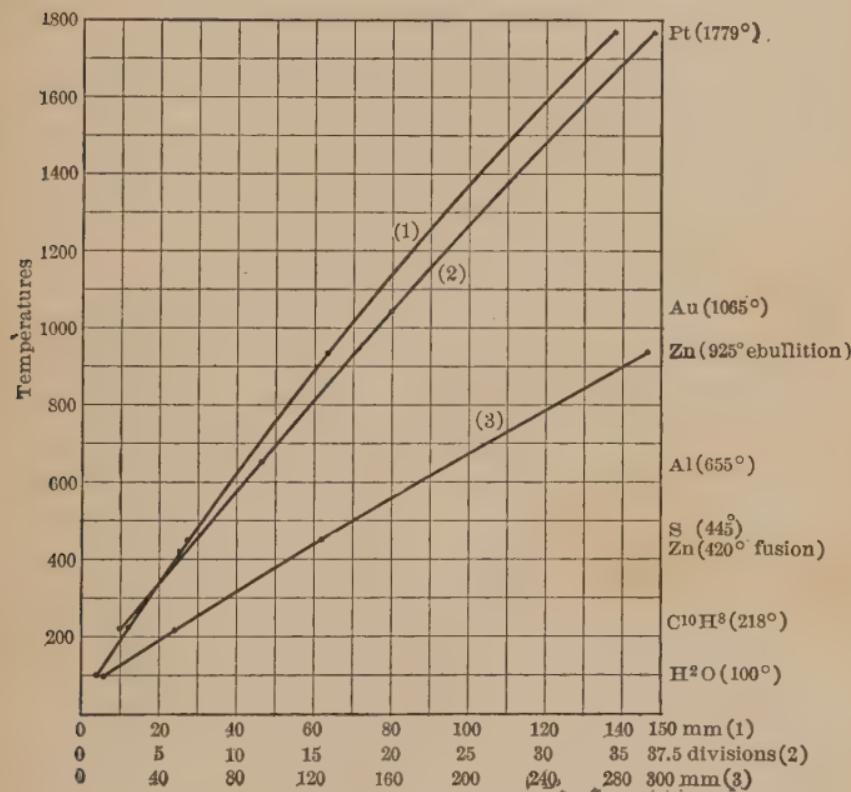


FIG. 37.

to begin by drying and dehydrating slowly this bullet to prevent its bursting. It is then placed in a flame sufficiently hot to bring about fusion of the metal; this flame should be very steady.

For the fusion of platinum a different process should be followed. One utilizes the fusion of the wires of the couple in the same operation which serves to make the

junction. Two observers are necessary, one to read the galvanometer and the other to note the fusion of the platinum. It is necessary to employ a flame sufficiently tall so that the temperature be regular throughout a considerable height. The junction of the two twisted wires is placed at a distance of at least 50 mm. above the blast-lamp nozzle, a strong blast of oxygen is turned on, and the gas-cock is opened gradually until fusion takes place. The same process should be used for the fusion of gold, with an air blast-lamp, on the condition that the flame of the latter be kept steady, which is not possible with bellows worked by foot. This method is, however, less precise than those that have been previously indicated.

We give here the curves of graduation (Fig. 37) of different couples, attached to different galvanometers or, in the case of the method of opposition (Poggendorf's method), to a Pouillet rheostat. In the last case the zero of graduation does not correspond to a zero electromotive force, and in consequence not to the temperature of the surrounding air, by reason of the supplementary resistance of a wire which was added to that of the rheostat.

	Fixed Points.	Mirror Galvanometer.	Pointer Galvanometer.	Method of Opposition.
Boiling water	100°	4.5 divs.		
Boiling naphthaline..	218	12 "	2.5 divs.	13 mm.
Melting zinc.....	420	26 "		
Boiling sulphur.....	445	28 "	123 "
Melting aluminium...	655	12 divs.	
Boiling zinc.....	925	64 divs.	294 "
Melting gold.....	1065	20 divs.	
Melting platinum....	1780	137.5 divs.	37 "	

Recent Researches.—The reliability of Holman's formula may also be illustrated by comparing his determinations of certain fixed points with more recently found values.

The two fixed points assumed by Holman, in his work with Lawrence and Barr, were the sulphur-point and the gold-point. Taking the S.B.P. = 445 and the gold-point = 1064, Holman's values of other points become, using his formula,

Al	Ag	Cu	Pt
654.7	962.7	1087	1760

The values determined by Holborn and Day are

Al	Ag	Cu	Au
657 to 654	961.5	1084	1064

These results should also be compared with Stansfield's, who worked with a Roberts-Austen recording-pyrometer, which he rendered still more sensitive by means of an auxiliary potentiometer, which balances the major part of the E.M.F. of the couple, the sensitive galvanometer being acted upon by only a small fraction of the thermo-current. The cold junction was kept in boiling water. He obtained

Al	Ag	Cu	Au
649.2	961.5	1083	1063

All of the above results go to show that the thermo-couple, made of relatively pure materials obtained from various sources, used under the most diverse experimental conditions, and its indications reduced by different methods, will nevertheless give results agreeing to 0.5 per cent or even closer over the range within which the thermo-couple can be used.

Electric Heating.—In recent years a great advance has been made in pyrometric practice in substituting for gas

furnaces those employing electric heating. This method was first used in pyrometric work for the determination of fixed points by means of the thermocouple by D. Berthelot in France and Holborn and Day in Germany. The earlier furnaces were constructed by winding pure nickel or platinum wire on porcelain tubes enclosed in an outer tube of porcelain and wrapped in asbestos. The nickel-wound furnaces may be used up to 1300° C. with care and they are readily rewound when burnt out. The platinum-wire furnaces are very expensive, but may be used up to 1500° C. These last have since been displaced by furnaces of the Heraeus type, which are made by winding platinum-foil of about 0.007 mm. thickness on porcelain tubes covered with an aluminium earth paste which does not attack platinum at high temperatures. These furnaces are inexpensive and very durable. Heraeus also manufactures iridium resistance furnaces with which temperatures over 2000° C. may be reached, and a very constant temperature maintained. A further advantage of the electric furnace is the absence of reducing gases.

The use of electric heating has rendered the standardization of the thermocouple and all other pyrometers an easy matter and increased greatly the accuracy attainable in establishing the fixed points in pyrometry.

Holborn and Day's Work.—In a series of painstaking researches carried out at the Reichsanstalt, these physicists, using electric heating, have succeeded in establishing many of the fixed points more exactly than had been previously done. We shall return to their work again in the chapter on standardization. They determined several points by two methods which they call the wire method and the crucible method. The former consists in inserting in the thermoelectric circuit between the platinum

and platinum-rhodium a centimeter of the wire (less than 0.03 gr.) of the material whose melting-point is sought, the junction thus modified being heated in an electric furnace until the metal melts, the E.M.F. being noted as the circuit breaks. With the crucible method a large mass—several hundred grammes at least—is heated in a crucible placed at the center of an electric furnace, whose temperature may be so nicely controlled that the freezing of 300 grm. of gold or copper, for instance, will take an hour or more. Both graphite and porcelain crucibles were used to test the effects of reducing and oxidizing surroundings. The metal in the graphite crucible is also covered with powdered graphite. The wire and crucible methods gave identical results with gold, whose melting-point they find to be 1064.0 ± 0.6 C. Copper wire in air gave 1065, so that either a copper or gold wire may be used to establish the same fixed point. Copper in graphite gives the freezing-point of 1084, however. The convenience of the wire method is offset by the contamination of the junction.

If a thermocouple, however well protected, is heated for a long time at a high temperature, its E.M.F. will change. It is well for accurate work to have at least two thermocouples, one of which is kept as a standard and only occasionally heated and never above 1200° C. In this way changes in the couple ordinarily used may be readily detected. Holborn, with Henning and Austin, has made a very complete study of the effects of continued heating in various atmospheres on the loss of weight and changes produced in electric and thermoelectric properties of the platinum metals. The following table shows the results of continued heating in air on the E.M.F. of the couples ordinarily used:

EFFECT OF PROLONGED HEATING ON E.M.F.

E.M.F. AGAINST PT IN MICROVOLTS.

Duration of Heating, Hours.	90 Pt—10 Ir.			
	700° C.	900°	1100°	1300°
0	16,540	19,740
3	9460	12,450	15,450	18,530
6	9160	11,930	14,780	17,640
8	8840	11,560	14,300	17,050

90 Pt—10 Rh.				
	800° C.	900°	1000°	1100°
0	7230	8340	9480	10,670
3	7250	8380	9510	10,690
6	7270	8400	9540
9	7280	8410	9540	10,720
12	7290	8420	9550

This investigation shows that the E.M.F. of a couple, and thus the indicated temperature, rise with continued heating, very considerably for a Pt—Ir couple and about 0.5 per cent for a Pt—Rh couple for ten hours' heating. The change is greatest during the first part of the heating. Before use, a thermocouple should be annealed by passing a current through it at a white heat, when future changes will be slight. This annealing also will restore to very nearly its normal value the E.M.F. of couples which have been in contact with silicates.

Changes in temperature distribution along the wire will also affect the apparent electromotive force of the couple, causing apparent changes in temperature as great as 20° at 1000° C. with the best wires obtainable. The less homogeneous the wires the more marked is this effect.

In the most exact work, therefore, the same conditions of immersion must be followed throughout, or the resulting changes in E.M.F. measured.

It follows from all this, as Holborn and Day state, that the temperature scale, once established, by means of the thermocouple, can be maintained with certainty only with the help of fixed temperatures such as the melting-points.

Industrial Applications.—The measurement of temperatures by thermoelectric couples has enhanced the accurate knowledge of a great number of high temperatures of which previously little or nothing was known. The measurements have been particularly numerous in the scientific and industrial investigations on iron. It is with the thermoelectric couple that Osmond and others, Roberts-Austen, Arnold, Howe, and Charpy have made all their studies on the molecular transformations of irons and steels. The conditions of manufacture and of treatment of these metals have been improved by the introduction into industrial works of this method of high-temperature measurements.

We give below, as examples, a series of determinations made by Le Chatelier in a certain number of industrial operations.

Steel.—Siemens-Martin open-hearth furnace:

Gas at the outlet of the gas-generator	720°
Gas at the entrance of the regenerator.....	400
Gas at the outlet of the regenerator.....	1200
Air " " " " "	1000
Interior of the furnace during refining.....	1550
Smoke at the foot of the chimney.....	300

Glass.—Basin furnace for bottles; pot furnace for window-glass:

Furnace.....	1400°
Glass in affinage.....	1310
Annealing of bottles.....	585
Drying of window-glass.....	600

Illuminating-gas.—Gazogène furnace:

Top of furnace.....	1190°
Base of furnace.....	1060
Retort at end of distillation.....	975
Smoke at base of regenerator.....	680

Porcelain.—Furnaces:

Hard porcelain.....	1400°
China porcelain.....	1275

Conditions of Use.—Thermoelectric couples, by reason of their easy use, ready calibration, small size, and of the precision of their indications, are preferable to all other pyrometric methods for ordinary investigations, scientific or industrial, and in fact they are almost the only ones employed to-day for such uses. Their employment, however, is not to be recommended for investigations of the highest precision; the preference should be given, as we have already said, to the electric-resistance pyrometer, within the range that this instrument can be used, when one possesses the means to graduate it with precision up to high temperatures. Above 1000° C. the thermocouple is the only form of electrical pyrometer which can be used; and attached to a suitable direct-reading galvanometer, this instrument is proving of great utility in the industries. In certain cases, which we shall discuss, a radiation or optical pyrometer may replace to advantage the thermoelectric.

Iridium-ruthenium Couple of Heraeus.—The upper limit for continued use of the platinum-rhodium couple is

about 1600° C. If a couple could be made of more refractory metals, higher temperatures might be measured. This has just been accomplished by Heraeus using a couple composed of pure iridium for one lead, and for the other an alloy of 90 parts iridium to 10 parts ruthenium, whose indications reach 2100° C.

Such a couple may be calibrated in terms of a rhodium couple up to 1600° and the platinum fusing-point may be taken by the wire method as a higher fixed point (1780°), but for still higher temperatures extrapolation of the E.M.F.-temperature relation must be resorted to.

Heraeus gives the following calibration of such a couple:

900° C.	2.95	millivolts
1000	3.32	"
1100	3.70	"
1200	4.08	"
1300	4.43	"
1400	4.78	"
1500	5.07	"
1600	5.32	"
1700	5.58	"
1780	5.75	"
1800	5.79	"
1900	5.99	"
2000	6.18	"
2100	6.36	"

The indications of this couple remain very constant with repeated heatings. The effect of heat conduction along the leads may cause an error as great as 50°, but this is readily eliminated by taking the platinum point.

The iridium-ruthenium couple has to be handled very carefully as it is excessively brittle.

Furnaces suitable for these high temperatures may be

made of chalk, magnesia, or iridium heated with an oxy-hydrogen flame. When chemical action is feared or complete freedom from gases is desired, an electrically heated iridium-tube furnace, also due to Heraeus, may be used.

Such iridium tubes as made by Heraeus have walls 0.2 to 0.3 mm. thick and carry from 500 to 1000 amperes at low voltage.

CHAPTER VII.

THE LAWS OF RADIATION.

General Principles.—The temperature of bodies may be estimated from the radiant energy that they send out, either in the form of visible light radiation or of the longer infra-red waves that are studied by their thermal effects. For the estimation of temperature in this way use is made of the so-called laws of radiation.

Temperature and Intensity of Radiation.—When we consider the enormous increase in the intensity of radiation with rise in temperature, this method appears especially well adapted to the measurement of high temperatures. Thus, for example, if the intensity of the red light ($\lambda=0.65\mu$) emitted by a body at 1000° C. is called 1, at 1500° C. the intensity will be over 130 times as great, and at 2000° C. over 2100 times as great.

The rapid increase of the photometric intensity of the light in comparison with that of the temperatures is shown by the following table, from Lummer and Kurlbaum, for light emitted by incandescent platinum. If I_1 and I_2 are the intensities of the light emitted at the absolute temperatures T_1 and T_2 (not differing many degrees from one another), then if we write

$$\frac{I_1}{I_2} = \left(\frac{T_1}{T_2}\right)^x.$$

The values of x at various absolute temperatures (T° C. + 273°) are as follows:

T° abs.	x .
900°	30
1000	25
1100	21
1200	19
1400	18
1600	15
1900	14

From this table it will at once be seen that at 1000° absolute (727° C.) the intensity of the light increases twenty-five times as rapidly as the temperature; at 1900° absolute (1627° C.) fourteen times as rapidly. The product $Tx=25000$ as shown by Rasch seems to express the relation between T and the exponent x .

Emissive Powers.—It would therefore appear that a system of optical pyrometry based on the intensity of the light emitted by incandescent bodies would be an ideal one, inasmuch as a comparatively rough measurement of the photometric intensity would measure the temperature quite accurately. This, however, is only partly true; it is limited somewhat by the fact that different bodies, although at the same temperature, emit vastly different amounts of light. Thus the intensity of the radiation from incandescent iron or carbon at 1000° C., for example, is many times greater than that emitted by such substances as magnesia, polished platinum, etc., at the same temperature. Consequently, if any conclusions were drawn as to the temperatures of these bodies from the light that they emit, it might lead to large errors. Thus at 1500° C. this difference in the intensity of the light emitted by carbon and by polished platinum would

lead to a difference in the estimated temperature of these bodies of about 100° C., and less at lower temperatures.

The "Black Body" of Kirchoff.—Kirchoff in one of the most important contributions to the theory of radiation was led to the important conception of what he termed a "*black body*," which he defined as one which would absorb all radiations falling on it, and would neither reflect nor transmit any. He further pointed out clearly the important fact that the radiation from such a black body was a function of the temperature alone, and was identical with the radiation inside an enclosure all parts of which have the same temperature. The first experimental realization of a black body as a practical laboratory apparatus was made by Lummer and Wien, by heating the walls of a hollow opaque enclosure as uniformly as possible and observing the radiation coming from the inside through a very small opening in the walls of the enclosure.

Experimental Realization.—No body is known whose surface radiation is exactly that of a black body. The radiations from such substances as carbon and iron approximate fairly near to black-body radiation, while such bodies as polished platinum and magnesia, etc., depart very far from it. Black-body radiations corresponding to temperatures from that of liquid air or lower, up to 1600° C. or higher (if suitable materials are chosen), are now available in the laboratory. For temperatures up to 600° or thereabouts, this is realized by immersing a metallic or other vessel in a constant temperature bath (liquid gas, vapor, or fused salt) and observing the radiation from the interior through a small opening in the walls. At higher temperatures it is very difficult to heat the walls of the enclosure uniformly, especially with gas-flames. Lummer and Kurlbaum have very satisfactorily overcome

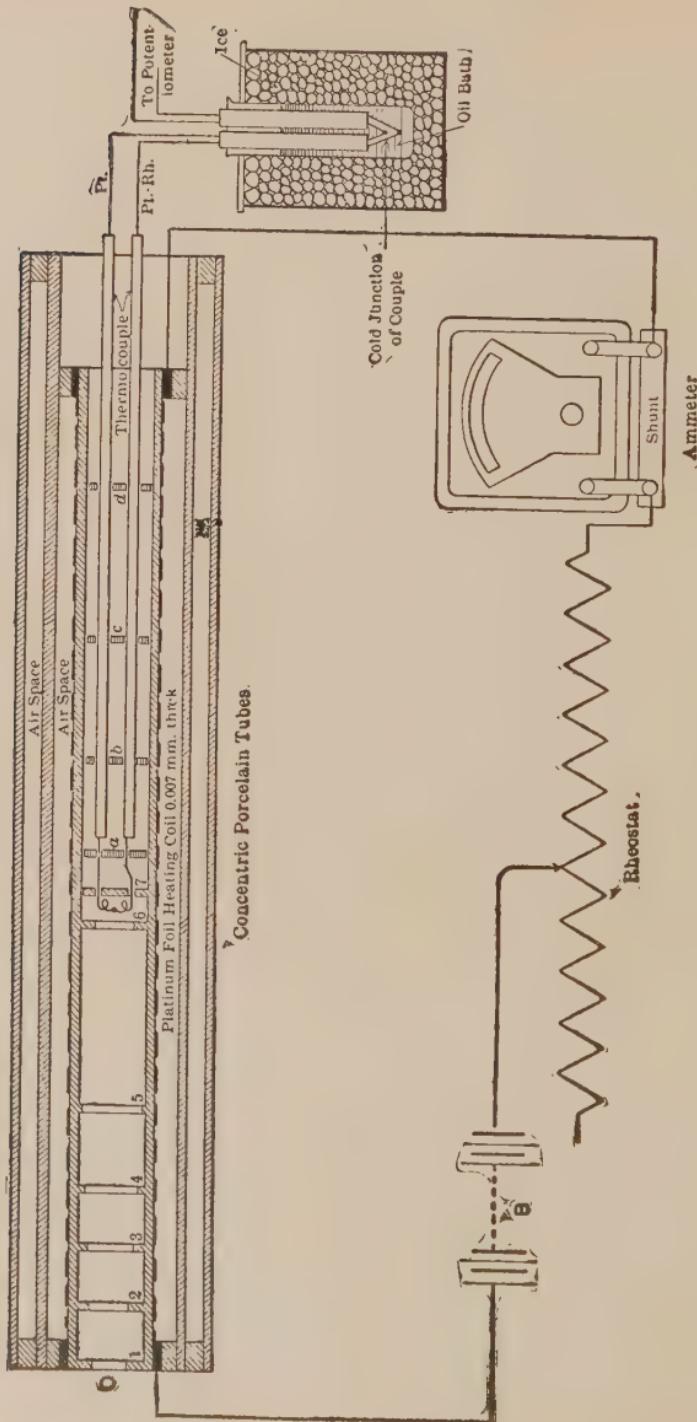


FIG. 38.

this difficulty in their electrically heated black body which is shown in section in Fig. 38.

The central porcelain tube is wound over with thin platinum-foil through which an electric current is sent which can be adjusted to maintain any desired temperature up to 1600° C. This tube is provided with a number of diaphragms to minimize the disturbing effects of air-currents. To protect this inner tube from external influences and to diminish unnecessary heat losses, it is surrounded by several porcelain tubes and air-spaces, as shown in the figure. The radiation from the uniformly heated region near the centre and which passes out through the end of the tube at O is a very close approximation of the ideal black-body radiation of Kirchoff. The temperature of this central region is measured by means of a carefully calibrated thermocouple.

As has already been stated, if magnesia, porcelain, platinum, iron, etc., are heated to the same temperature, they will emit vastly different amounts of light. If, however, these bodies * are heated inside a black body, they will all emit the same radiation, and on looking into the small opening all details of their contour will be lost, the whole region being of uniform brightness. Thus, in the black body described above, before the heating has become uniform, the platinum wires of the thermocouple can be seen as dark lines against the brighter background, but when the heating current has been maintained constant for some time, so that the heating has become uniform in the inner central chamber, the wires of the couple almost completely disappear, notwithstanding that, of all sub-

* It is here assumed that the radiation is purely thermal and that no part is due to luminescence, as the laws of radiation are only directly applicable where such is the case.

stances, platinum and the black oxide of the radiating walls differ most widely in their radiating powers (emissivities).

Realization in Practice. — Fortunately in pyrometric practice it is often easy to realize very nearly the conditions of a black or totally absorbing body. Thus the interior of most furnaces, kilns, and ovens approximates this condition, or the bottom of a closed tube of any material thrust into any space heated to incandescence. Again, iron and coal observed in the open are not far removed in their optical properties from the black body.

Black-body Temperature. — The term black-body temperature has come into quite extensive use and is of great convenience in the discussion of pyrometric problems. The temperatures indicated by a radiation-pyrometer that has been calibrated against a black body are known as black-body temperatures. Thus, were a piece of iron and a piece of porcelain both at 1200° , the optical pyrometer, which used the red light emitted by these bodies, would give, as the temperature of these bodies, 1140° and 1100° respectively. This means that iron and porcelain at 1200° emit red light of the same intensity as is emitted by a black body at 1140° and 1100° C. respectively. The "black-body temperature" of these materials for green light might differ quite appreciably from that for red light. It is at once evident that if the "black-body temperatures" of different bodies, *e.g.*, carbon and platinum, are equal, their actual temperatures may differ considerably (180° C., or so, at 1500° C.). This violates our ordinary conception of equal temperatures, which is based on thermal equilibrium between the bodies if brought into contact.

The temperature of any body, therefore, as measured by an optical pyrometer will always be lower than its true temperature by an amount depending on the depar-

ture of its radiation from that of a black body. There is another source of error, however, that may act in the direction of making the pyrometer read too high, due to light reflected by the body whose temperature is being measured. This source of error may very often be eliminated, where the accessibility of the work permits, by running a tube down to the incandescent surface, which will cut off stray radiation from the surrounding flames. The magnitude of the error that may arise from light reflected from surrounding hotter objects may be quite considerable (several hundred degrees), depending on the temperature, area, and position of the surrounding hot objects and the reflecting power of the surface whose temperature is under observation.

LAWS OF RADIATION.

Stefan's Law.—Naturally the first relation sought between intensity of radiation and temperature was one for the total radiation energy sent out by a body, as it required less delicate instruments for measurement than the study of the spectral distribution of energy. Numerous attempts to express such a relation were made by Newton, Dulong and Petit, Rosetti, and others. These attempts, however, merely resulted in empirical expressions that held only through narrow ranges of temperature. The first important step was made by Stefan, who examined some of the experimental data of Tyndall on the radiation of incandescent platinum wire in the interval 525° C. to 1200° C., and was led to the conclusion that the energy radiated was proportional to the fourth power of the absolute temperatures. This relation seemed to be further supported by the best experimental data of other observers, at least to within the limit of accuracy of their observations, being strictly true, however, only

for the energy of total radiation from a black body. This relation received independent confirmation from Boltzmann, who deduced it from thermodynamic reasoning. The conditions imposed by Boltzmann in his discussion on the nature of the radiation were such as are fulfilled by the radiation from a black body. This relation, which has now come to be generally known as the *Stefan-Boltzmann radiation law*, may then be stated as follows:

The energy radiated by a black body is proportional to the fourth power of the absolute temperature, or

$$E = K(T^4 - T_0^4),$$

when E is the total energy radiated by the body at absolute temperature T° to the body at absolute temperature T_0° , and K is a constant depending on the units used. This law has received abundant experimental support from the researches of Lummer, Kurlbaum, Pringsheim, Paschen, and others, throughout the widest range within which temperature-measurements can be made.

An illustration of the experimental evidence in support of this law is given in the table taken from the experiments of Lummer and Kurlbaum:

Absolute Temperature.		$K = \frac{E}{T^4 - T_0^4}$		
T	T_0	Black body.	Polished Platinum.	Iron Oxide.
372.8	290.5	108.9
492	290	109.0	2.28	33.1
654	290	108.4	6.56	33.1
795	290	109.9	8.14	36.6
1108	290	109.0	12.18	46.9
1481	290	110.7	16.69	65.3
1761	290	19.64

It will also be seen from this table that while the intensity of the total radiation of iron oxide is 4 or 5 times that of polished platinum, it is still considerably less than that emitted by a black body. The total radiation from bodies other than a black body increases more rapidly than the 4th power of the absolute temperature, so that as the temperature is raised the radiation of all bodies approaches that of the black body.

Laws of Energy Distribution.—Among the first facts to be noticed about the nature of the radiations sent out by bodies were, that at low temperatures these radiations consisted of ether waves too long to affect the human eye. As the temperature was raised, shorter and shorter waves were added which could finally be detected by the eye; the first of the visible radiations producing the sensation termed red, then orange, etc., until the violet waves were reached, which were the shortest waves that the eye could detect.

Soon after Langley brought out the bolometer, which was so admirably adapted to the measurement of the minute energy of radiations, a great mass of valuable experimental data was obtained, bearing on the spectral distribution of the energy of the radiation emitted by various bodies. Among the most important of these contributions must be mentioned the researches of Paschen, who examined the distribution of energy in the emission and absorption spectra of various substances. Among the experimental facts established by these researches were, that by far the largest portion of the energy in the spectrum was found in the infra-red region, that the position of the wave length having the maximum energy depended on the temperature of the body, and that, as the temperature was raised, the energy of all the waves emitted increased, but the shorter waves more

rapidly than the longer, so that the position (wave length) of maximum energy in the spectrum shifted toward shorter wave lengths. These facts are well illustrated

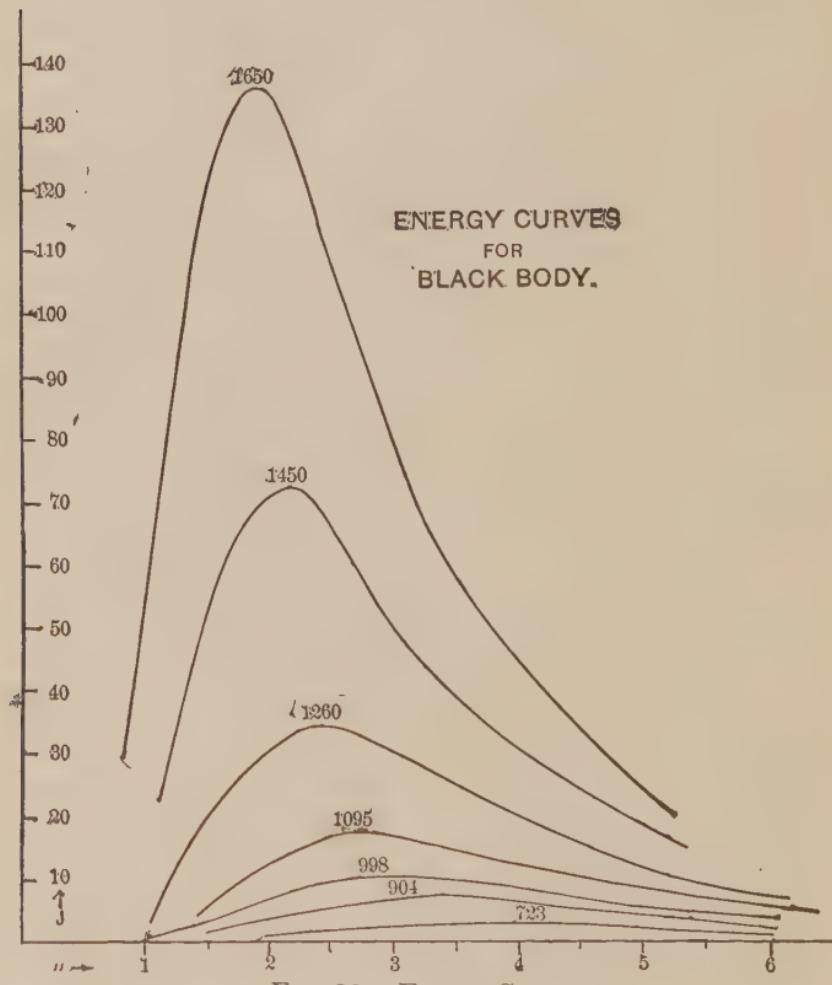


FIG. 39.—Energy Curves.

by the curves shown in Fig. 39, taken from a paper by Lummer and Pringsheim, in which the ordinates are proportional to the intensity of radiation emitted by a black body, and the abscissas are wave lengths (in thousandths

of a millimeter). Such curves, as are here shown, where the temperature is constant and the energy is measured corresponding to radiations of different wave lengths emitted by a body, are called *energy curves*, *i.e.*, the relation determined is $J=f(\lambda)$ for $T=\text{constant}$, where $J=\text{energy}$ corresponding to wave length λ , strictly the energy comprised in the region of the spectrum between λ and $\lambda+d\lambda$, and T is the absolute temperature of the radiating source. It is also interesting to study the change in the intensity of some particular wave length as the temperature of the radiating source is changed, *i.e.*, to find $J=F(T)$ for $\lambda=\text{constant}$. This can of course be done by exposing the bolometer strip in a fixed part of the spectrum and observing the galvanometer deflections as the temperature is changed. The curves in this way for $J=F(T)$ are called *isochromatic curves*.

Wien's Laws.—Wien was led from theoretical considerations to state that “when the temperature increases, the wave length of every monochromatic radiation diminishes in such a way that the product of the temperature and the wave length is a constant,”

$$\lambda T = \lambda_0 T_0.$$

Hence for the wave length of the maximum energy, λ_m , we have

$$\lambda_m T = \text{const.} = 2930. \dots \quad (I)$$

This is known as the “Wien displacement law” and is simply a mathematical statement of the fact that as the temperature of the radiating source is changed the wave length having maximum energy in the spectrum will be changed in such a way that the product of this wave length and the corresponding absolute temperature of

the source, T , is equal to a constant. Wien then combined the above relation with the Stefan-Boltzmann law and was led to the relation that

$$E_{\max} T^{-5} = \text{constant} = B, \dots \quad (\text{II})$$

in which E_{\max} indicates the energy corresponding to the wave length of the maximum energy and T is the absolute temperature of the radiating source (black body). Both of these generalizations of Wien for the radiations emitted by a black body have received the most convincing experimental verification throughout the widest ranges of measurable temperatures that are at present available to the experimentalist.

As an illustration of the experimental evidence in support of these two laws of radiation, the following table has been added, taken from a paper by Lummer and Pringsheim on the radiation from a black body:

λ_m	E_m	$A = \lambda_m T$	$B = E_m T^{-5}$	Absolute Temperature.	$T = \sqrt[5]{\frac{E_m}{B_{\text{mean}}}}$	Diff.
4.53	2.026	2814	2190.10^{-17}	621°.2	621.3	+0°.1
4.08	4.28	2950	2166	723	721.5	-1.5
3.28	13.66	2980	2208	908.5	910.1	+1.6
2.96	21.50	2956	2166	998.5	996.5	-2.0
2.71	34.0	2966	2164	1094.5	1092.3	-2.2
2.35	68.8	2959	2176	1259.0	1257.5	-1.5
2.04	145.00	2979	2184	1460.4	1460.0	-0.4
1.78	270.8	2928	2246	1646	1653.5	+7.5
Mean	2940		2188.10^{-17}			

As will be seen, these results of experiment are in most satisfactory agreement with these laws, when one considers the experimental difficulties that are involved in the measurements. In the value for B the tempera-

ture enters to the 5th power, so that a small error in the temperature produces a very marked effect on the value of B . Paschen later obtained $\lambda_m T = 2920$.

Wien also published the result of a further theoretical investigation on the spectral distribution of energy in the radiation of a black body, in which he was led to the conclusion that the energy J corresponding to any wave length was represented by

$$J = c_1 \lambda^{-5} e^{-\frac{c_2}{rT}}, \dots \quad \text{(III)}$$

where J is the energy corresponding to wave-length λ , T is the absolute temperature of the radiating black body, e is the base of the natural system of logarithms, and c_1 and c_2 are constants.

The subsequent experimental work of Beckman, Rubens, and others has shown that Wien's distribution law does not hold for long wave lengths, although it amply suffices throughout the whole visible spectrum, and may be applied in all cases where $\lambda T < 3000$.

Planck has deduced an expression analogous to Wien's which applies with exactness for all wave-lengths and temperatures. His law, which reduces to Wien's for small values of λ , may be written

$$J = c_1 \lambda^{-5} \left(e^{\frac{c_2}{rT}} - 1 \right)^{-1}.$$

Other radiation laws have also been suggested, but Planck's seems to best satisfy both experiment and theory.

For the radiation from all substances that have been

examined experimentally, it has been found that the "displacement law,"

$$\lambda_{m1} T = \text{const.} = A_1, \dots \quad (\text{Ia})$$

still holds true, although the radiation may depart far from that for a black body. In this case, however, the value of the constant is different from that for a black body. Thus for polished platinum Lummer and Pringsheim found $A_1 = 2626$.

For the radiation from other than a black body the law of maximum energy applies only in the modified form

$$E_m T^{-\alpha} = \text{const.} = B_1, \dots \quad (\text{IIa})$$

where α cannot be less than 5 and is not probably ever greater than 6, the value found by Lummer and Pringsheim for polished platinum. The general form of Wien's

law III takes the form $J = c_1 \lambda^{-\alpha} e^{-\frac{c_2}{\lambda T}}$; where $6 > \alpha > 5$.

Lummer and Pringsheim found the following limits of temperature as given by the Wien relation Ia:

	λ_m	T_{\max}	T_{\min}
Electric arc.	0.7 μ	4200 abs.	3750 abs.
Nernst lamp.	1.2	2450	2200
Auer burner.	1.2	2450	2200
Incandescent lamp.	1.4	2100	1875
Candle.	1.5	1960	1750
Argand burner.	1.55	1900	1700

Lummer and Pringsheim also heated a carbon tube electrically to about 2000°C . and observed the temperature inside simultaneously with instruments making use of the several radiation laws;

Method.	T absolute.
Photometric.	$\left\{ \begin{array}{l} 2310 \\ 2320 \\ 2330 \end{array} \right.$
Total radiation.	$\left\{ \begin{array}{l} 2330 \\ 2345 \\ 2325 \end{array} \right.$
Energy maximum.	$\left\{ \begin{array}{l} 2330 \\ 2320 \end{array} \right.$

This complete concordance at such a high temperature between the different radiation methods gives further confidence in the legitimacy of their indefinite extrapolation for non-luminescent bodies. Waidner and Burgess have also found that this accord probably exists at the temperature of the electric arc, 3600° C.

Applications to Pyrometry.—It is evident that theoretically any of these laws and their various consequences might be used as a basis of pyrometry, but practically it is not convenient to make use of all of them. The displacement law ($\lambda_m T = A$) and the maximum-energy law ($E_m T^{-5} = B$) of Wien are well-established relations, but in practice it is exceedingly difficult to construct instruments of sufficient sensibility to give any considerable precision, and any industrial pyrometer using these principles is out of the question at the present time. The reason of the lack of sensibility with the relation $\lambda_m T = A$ is due to the fact that the exact position of the wave length possessing the maximum of energy is very difficult to locate, especially at relatively low temperatures; see Fig. 39. The value of the maximum energy could perhaps be measured more readily, but, as this quantity varies as the fifth power of the temperature, there would hardly be any preference for this over the former method.

There have been, however, several most convenient, simple, and very accurate instruments devised which are

based either on the use of Stefan's law $(E = K(T^4 - T_0^4))$ or Wien's distribution law $(J = c_1 \lambda^{-5} e^{-\frac{c_2}{\lambda T}})$, either directly or indirectly, and in the two following chapters we shall treat of these at some length.

Crova suggested that the upper limit of the spectrum of an incandescent body might be used as a measure of this temperature, and Hempel has recently tried this method with a special form of spectroscope, using a luminescent screen for observing when the upper spectrum limit is beyond the visible radiations; but, as compared with the photometric and radiation pyrometers, only crude results can be obtained.

CHAPTER VIII.

HEAT-RADIATION PYROMETER.

Principle.—The quantity of heat that a body receives by radiation from another body depends on certain conditions relative to each of the two bodies, which are:

1. Temperature;
2. Surface;
3. Distance apart;
4. Emissive and absorbing power.

In order to utilize heat radiation for the determination of temperatures, one measures a heat change produced on the body used as an instrument by the body to be studied; this heat change is either a rise of temperature or a resulting phenomenon, such as a change of electrical resistance, thermoelectromotive force, etc.

The quantity of heat given off is proportional to the radiating surface S , and varies inversely as the square of the distance l .

$$q = k \frac{S}{l^2} = k' \frac{d^2}{l^2} = k'' E \cdot \frac{d^2}{l^2},$$

d being the diameter of the radiating surface S , E its emissive power.

Now, $\frac{d}{l}$ is the apparent diameter of the object; the quantity of heat radiated depends then upon the solid angle under which the object is seen. Any instrument

making use of the intensity of radiation must, therefore, have a receiving device of sufficiently small area so that it may be completely covered by the desired radiation.

The emissive power E is very variable from one substance to another as we have seen, and for the same substance variable with the temperature. It would be desirable to determine this, but that is difficult, often impossible, especially at high temperatures, although some advance has been made in this direction as we have seen in the preceding chapter.

The coefficient k'' is a function of the temperature alone, which expresses the law of variation of the radiation with the temperature. This law should be determined in the first place. It is on the more or less exact knowledge of this law that the entire accuracy of the results depends. We have seen that Stefan's law (p. 177) satisfies all requirements for the measurement of total radiation, although the early experimenters, working before the establishment of this law, were obliged to express their results empirically.

Let us see now what are the experimental arrangements which have been used to measure the intensity of heat radiation; these measurements have had for their only aim, until recently, the determination of the sun's temperature, but they may serve other uses.

Pouillet's Experiments.—Before Pouillet, Gasparin had already made some trials. His apparatus consisted of a hollow brass sphere mounted on a foot and blackened; a thermometer was used to measure the rise in temperature of the water contained in the sphere. The advantage of this arrangement was that the apparatus was always turned properly toward the sun.

The *pyrrhéliomètre* of Pouillet consists of a calorimeter which measures directly the heat received by radiation

(Fig. 40). A very thin silver box is carried by a hollow tube, cut along a generatrix to let the thermometer be seen. The box is of 100 mm. diameter by 15 mm. height; it contains 100 cc. of water. At the lower part of the box is located a metallic disk of the same diameter as the box, and serving to turn the apparatus toward the sun; it suffices, in fact, for the shadows of the box and disk to coincide exactly in order that the system be properly pointed. A knob serves to turn the apparatus about its axis in order to stir the water. Finally a support gives the means of placing the system in any desired orientation.

To take an observation, the apparatus is set up and shielded from the sun's action by means of a screen; the readings of the thermometer are taken for five minutes; the screen is removed and the thermometer is read for five minutes; the screen is put back, and a new set of readings of the thermometer for five minutes is taken.

The first and the third sets furnish the corrections due to the surroundings. Pouillet observed in this way a rise of temperature of 1° in five minutes.

In the determination of the temperature of the sun it was evidently necessary to take into account the heat absorbed by the atmosphere (it is about 20 per cent of the total radiation from the sun). Pouillet found by this method 1300° for the temperature of the sun.

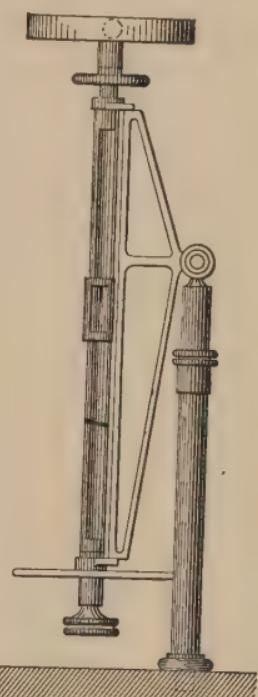


FIG. 40.

Experiments of Violle.—Violle makes use of an *actinomètre*, whose principle is quite different from that of the preceding apparatus; one observes the stationary equilibrium of a thermometer receiving simultaneously radiation from an enclosure at fixed temperature, and that from the hot substance to be investigated (Fig. 41).

The apparatus consists of two spherical concentric coverings of brass, in which a water circulation may be set up at constant temperature, or ice may be substituted for water. The inner covering of 150 mm. diameter is blackened inside. The thermometer has a spherical bulb whose diameter varies from 5 to 15 mm.; the surface of

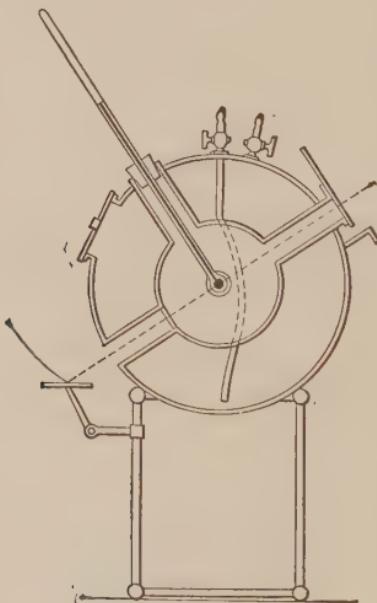


FIG. 41.

the bulb is also blackened. The scale is divided into fifths of a degree. The entrance-tube carries a diaphragm pierced with holes of different diameter; on the extension of this tube is located an opening closed by a ground-

glass mirror slightly blackened, which permits of determining that the solar rays fall quite exactly upon the thermometer bulb.

The establishment of the temperature equilibrium requires fifteen minutes, and the differences of temperature observed vary from 15° to 20° .

Violle found in this way, for the temperature of the sun, figures varying from 1500° to 2500° .

Pouillet and Violle made use of Dulong and Petit's law of radiation,

$$q=a',$$

that the discoverers had established by observations reaching only to 300° .

The constant a may be determined for each apparatus by a single experiment made at a known temperature. This law, as we shall show farther on, is not exact, so that, according to the temperature used to determine the constant, a different value of the latter is found, and consequently also different values at temperatures calculated, assuming this law to hold. This is the reason for the differences between the three figures, 1300, 1500, and 2500, of Pouillet and Violle. They correspond to determinations of the constant obtained by means of preliminary experiments made at the temperatures of 100° , 300° , and 1500° .

The elder Secchi, making use of Newton's formula,

$$q=a(t_1-t_0),$$

still more inexact, found for the sun's temperature several millions of degrees.

Work of Rosetti.—The Italian scientist, Rosetti, was the first to grasp the fundamental importance of the choice

of the law assumed for radiating power; he showed that a graduation made by an experiment at 300° gave for the temperature of a body heated in the oxyhydrogen flame:

46,000 if one uses the law of Newton;

1,100 " " " " " Dulong and Petit.

Now the temperature of the oxyhydrogen flame is about 2000° .

This physicist used a thermoelectric pile whose sensibility could be changed without touching the element; in the apparatus of Violle it is necessary, on the contrary, to change the thermometer, a proceeding which renders the observations comparable with difficulty.

The pile (Fig. 42) consists of twenty-five sheets of bismuth and antimony; these sheets are very thin, for the whole of the apparatus is but 5 mm. on a side. The whole is enclosed in a small metallic tube.

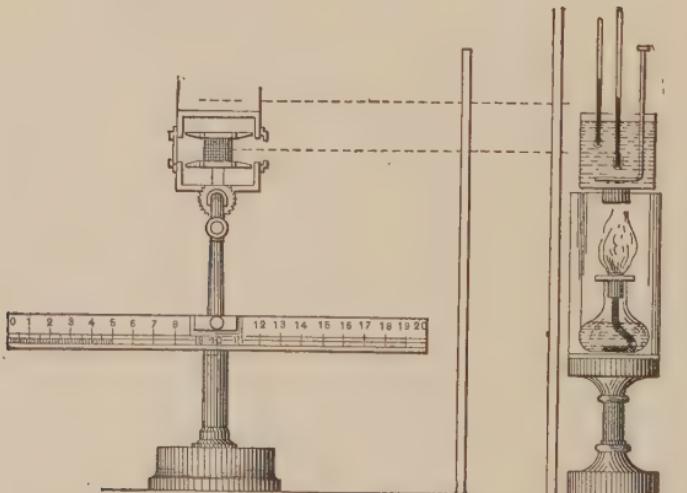


FIG. 42.

To make an experiment there is placed before the pile a screen filled with water, which is removed at the instant of taking an observation.

A preliminary calibration made with a Leslie's cube of iron filled with mercury that is heated from 0° to 300° gave the following results:

Excess of the Temperature of the Cube over the Surround- ing Temperature.	Reading of Galvanometer.
32°.8.....	10°
112 .8.....	55
192 .8.....	141 .9
272 .8.....	283 .5

Newton's law and that of Dulong and Petit giving no concordance between the numbers observed and those computed, Rosetti proposed the formula

$$Q = aT^2(T - \theta) - b(T - \theta),$$

where T = absolute temperature of the radiating body, θ = the absolute temperature of the surroundings. This formula with two parameters permits necessarily a closer following of the phenomenon than a formula with but a single parameter.

$T - \theta$	Deflections Observed.	Deflections Computed.	
		Dulong's Law.	Rosetti's Law.
50	$A = 17.2$	$A + 2.12$	$A - 0.23$
100	46.4	+0.95	
150	90.1	-2.12	+0.70
200	151.7	+4.82	+0.99
250	234.7	+2.83	-0.12

Rosetti showed later that the formula he proposed did not lead to absurd results for higher temperatures. A mass of copper was heated to redness in a flame, and the temperature was estimated by the calorimetric method (a quite uncertain method, as the variation of the specific heat of copper is not known). The two methods gave

respectively 735° and 760° . This difference of 25° is less than the experimental uncertainties.

Disks of blackened metal placed in the upper part of a Bunsen flame gave, according to the formula, temperatures of the order of 1000° ; oxychloride of magnesium in the oxyhydrogen blast-lamp gave 2300° . All these numbers are possible.

Rosetti, using this formula, found $10,000^{\circ}$ for the temperature of the sun, this figure resulting from an extrapolation above 300° .

Experiments of Wilson and Gray.—These physicists measured the intensity of radiation by means of a thermo-electric couple, a method first conceived by Deprez and d'Arsonval. A movable coil made of two different metals (silver and palladium) is suspended by a silk cocoon fibre between the poles of a magnet. The solar radiation is allowed to fall upon one of the junctions, while upon the other junction is directed a source of heat which exactly balances the first. As the temperature of this auxiliary source is necessarily the lesser, it is necessary that the apparent angle which it subtends at the galvanometer be the greater.

Wilson and Gray used an apparatus similar to the radiometer of Boys. The suspending fibre is of quartz; the metals employed are bismuth and antimony: the electromotive force so produced is twenty times greater than that obtained with the palladium-silver couple. The metallic strips R and R' (Fig. 43) are very thin (0.1 mm.), which renders the construction of the apparatus quite delicate. In order to protect the movable coil against air-currents, it is enclosed in a metallic case (Fig. 44); an open tube lets pass in the radiation; diaphragms set inside this tube prevent air-disturbances.

Instead of measuring, as may be done, the deflection of

the mobile parts, the investigators preferred to employ a null method making use of another radiation, that from a modification of the *meldometer* of Jolly, an apparatus used also for the graduation of the radiomicrometer. The

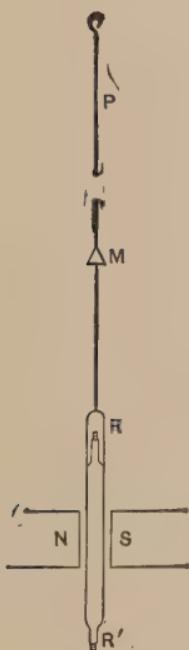


FIG. 43.

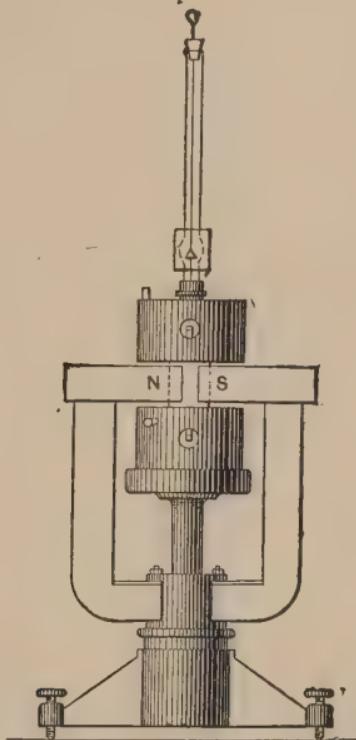


FIG. 44.

meldometer (Chapter X) consists of a strip of platinum heated by an electric current; the dimensions are as follows: 102 mm. in length, 12 mm. in breadth, and 0.01 mm. thick. This strip they placed in the midst of an enclosure surrounded by water. Fastened at one end, it is held in place at the other end by a spring and carries on this end a lever to which is fixed a mirror arrangement serving to optically amplify the variations in the length of

the strip resulting from its heating by the passage of the more or less intense current.

The relation between the change of length and the temperature is determined by means of the fusion of very small fragments ($1/10$ milligramme) of bodies whose fusing-points are known. Wilson and Gray used the following, which for the gold and palladium are certainly too low:

Silver chloride.....	452°
Gold.....	1045
Palladium.....	1500

With this apparatus they apparently verified, up to the fusion of platinum, the law of radiation given by Stefan,

$$E = k(T^4 - T_0^4).$$

For the purpose of graduation, the meldometer was removed to a distance, so that its action on the radiomicrometer was always the same, and it was assumed that the intensity varies as the inverse square of the distance. It is besides necessary to know the emissive power of platinum; Wilson and Gray took as starting-points the results given by previous experiments:

t°	Emissive Power.
300°	$\frac{1}{5.4}$
600	$\frac{1}{4.2}$
800	$\frac{1}{3.9}$

And by extrapolation they found $1/2.9$ at the temperature of 1250° , temperature which balanced the solar radiation, with the somewhat large apparent angle subtended by the meldometer. In admitting, then, with Rosetti and Young, a zenith absorption of 30 per cent, the temperature of the

sun, supposed to be a black body, was found equal to about 6200° .

This figure must be considerably uncertain, on account of the errors involved in the fusing-points employed for graduation, and because of the fact that the radiation from platinum does not obey Stefan's law. Furthermore the constants for platinum were found in terms of those of copper oxide, a substance they found, incorrectly, to depart more from a black body than polished platinum.

Langley and Abbot's Experiments.—Langley has devised, under the name of bolometer, a radiometric apparatus which he has used only incidentally to measure temperatures, but which may be so used and has the advantage over the preceding methods of being more sensitive.

It consists of a Wheatstone bridge, one arm of which is made of flat wires extremely thin (0.01 mm.) and very short (a few millimeters at the most). The variations of resistance of this arm of the bridge submitted to the radiation are measured. The current passing through the system is capable of raising its temperature 3° or 4° ; the excess of heat furnished to one of the arms produces a deflection of the galvanometer.

The system is fixed at the bottom of a tube which may be pointed like a telescope toward the body whose radiation is to be measured; diaphragms fixed at various points stop interior currents of air. One may also, by aid of a lens, concentrate the radiation upon the wire and amplify very much in this way the effect produced when the apparent angle of the object is small.

The bolometer of Langley has up to the present been used almost exclusively to study the distribution of radiant energy in the solar spectrum, and especially in the infra-red. It is sufficiently sensitive in the hands of

Langley and Abbot to detect changes of less than 0.000001 C.

Conditions of Use.—We have dwelt at length upon those radiation-pyrometers which have been used up to the present only for a single purpose, the estimation of the sun's temperature, because it is possible that some day or other their usage may penetrate into industrial works, where they may be of real service. In a certain number of industrial operations the temperatures are so high that no substance, not even platinum, can resist for long their action. When it is desired to have apparatus of continuous indications, and at the same time unalterable, it will be necessary to make use of radiation-pyrometers.

A tube of fire-clay passing through the lining of the furnace, and penetrating into the midst of the latter for a distance of 0.50 m. to 1.00 m., closed at the inner end and open at the outer, would give a radiating surface at the temperature of the furnace which could be examined by means of a lens projecting upon the measuring apparatus the image of the sealed base of this tube. This arrangement also gives radiation obeying very nearly the laws we have discussed, that is, a black body is realized approximately and Stefan's and Wien's laws may be used with radiation instruments.

Féry Thermoelectric Telescope.—This pyrometer is the only convenient form of instrument making use of total radiation and based on Stefan's law (p. 177) which has come into practical use for temperature-measurements. As in the case of the photometric pyrometers, the limitations as to the realization of a black body apply here also.

Use is made of the Stefan-Boltzmann law,

$$E = k(T^4 - T_0^4),$$

in the following way: Radiation from an incandescent

body is focussed upon a very sensitive thermocouple and raises its temperature. The electromotive force thus generated at the junction actuates a sensitive potential galvanometer in series with the couple in exactly the same way as in the Le Chatelier thermoelectric pyrometer; so that we have here a radiation-pyrometer which is direct-reading by means of a pointer on a scale, and may therefore readily be made a recording instrument.

The difficulty in construction of such an instrument is realizing a material for lens which is transparent for all radiations visible and invisible, so that the pyrometer may be calibrated directly in terms of Stefan's law and so that its indications will be reliable at temperatures however high. This is effected by use of a fluorite lens which for temperatures above 900° C. satisfies the conditions of not altering appreciably the radiations transmitted through it; that is to say, the ratio of the radiations absorbed to the radiation transmitted is constant.

At low temperatures a large proportion of the energy exists in the form of long wave lengths, and as fluorite has an absorption-band in the infra-red (near 6μ), it will absorb a considerable proportion of the radiation, and therefore Stefan's law can no longer be assumed.

Fig. 45 illustrates the construction of the instrument, where F is the fluorite lens, P a rack and pinion for focusing the radiations upon the thermo-junction of iron-constantan, and protected from extraneous rays by the screens C , D , shown also in section at AB . The thermo-junction is of exceedingly small dimensions, only a few thousandths of a millimeter wide, and is soldered to a silver disk. The leads are brought out to the insulated binding-posts b , b' , so placed as to reduce the chances of extraneous thermal currents to a minimum. The circuit is completed through a sensitive galvanometer provided with a scale. A dia-

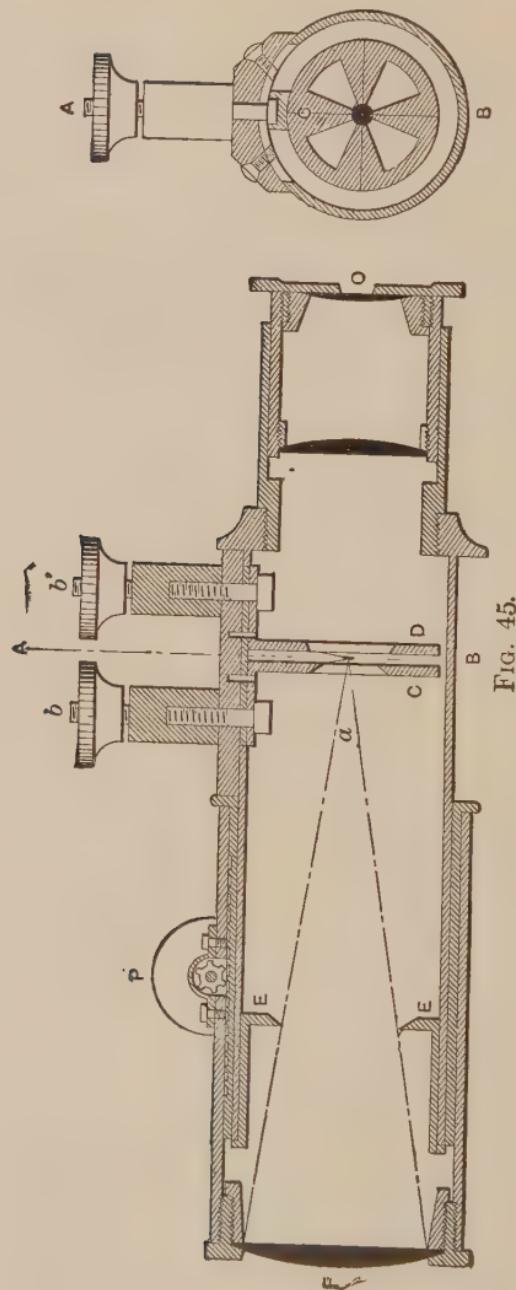


FIG. 45.

phragm fixed in size and position, EE , gives an opening of constant angle independent of the focussing whereby the cone of rays striking the junction is not changed in size by focussing.

In making a temperature-measurement it is necessary to sharply focus the image of the incandescent object upon the thermo-junction by means of the eye-piece O , and care must be taken that this image is of greater size than the junction. This adjustment once made, the pyrometer functions indefinitely while sighted upon the same object, and readings of the galvanometer scale give temperatures directly from the calibration.

The precision attainable with this form of instrument, over the range it may be controlled with the thermoelectric pyrometer, is shown from data obtained by Féry, assuming Stefan's law to hold in the form,

$$CE = d = 7.66T^4 \times 10^{-12},$$

where E is the total energy of radiation and d the galvanometer deflection and T the absolute temperature.

d	Temp. from Thermocouple.	Temp. from Stefan's Law.	Δ in Degrees.	Error in %.
11	844°	860°	+16°	1.85
14	914	925	+11	.84
17.7	990	990	0	.0
21.5	1054	1060	+ 6	.60
26.0	1120	1120	0	.0
32.2	1192	1190	- 2	.17
38.7	1260	1250	-10	.80
45.7	1328	1320	- 8	.60
52.5	1385	1380	- 5	.36
62.2	1458	1450	- 8	.50

It is evident, furthermoré, that if the galvanometer has a uniformly graduated scale and the temperature T_1 corresponding to any one scale reading R_1 is known, that for

any other reading R_2 may be found from the relation

$$T_2 = T_1 \sqrt[4]{\frac{R_2}{R_1}},$$

which also shows that errors in the galvanometer readings are divided by four when reduced to temperatures. For very high temperatures deflections off the scale of the galvanometer will be obtained. Féry overcomes this difficulty by substituting a smaller diaphragm before the objective when the radiation is reduced in the ratio of the areas of the apertures. Shunting the galvanometer will also accomplish the same end, and this latter method is probably capable of more accuracy than Féry's.

The highest temperatures which may be estimated by this pyrometer are limited only by the applications of Stefan's law to this extreme region, and whether Stefan's law applies or not, consistent results, nevertheless, will be obtained.

The laboratory form of apparatus described above is not suitable for use in technical practice, and fluorite is difficult to get of sufficient size. An industrial pyrometer is readily made by substituting for the fluorite lens one of glass, and for the delicate galvanometer one of the same type and sensibility as used in thermoelectric work; the resulting instrument is robust and sufficiently sensitive for all practical uses and as made has a range of from 800° C. to 1600° C., although the upper limit could readily be extended by having two scales on the instrument, with a shunt.

The indications of the industrial form of this pyrometer will not obey Stefan's law, but the instrument may readily be calibrated by direct comparison either with a thermocouple or with a laboratory form of Féry instru-

ment, and the scale of temperatures engraved on the instrument.

Both types of instrument can be used to reach lower temperatures (650°) by means of more sensitive galvanometers.

Lower temperatures might also be reached by converting the instrument into a reflecting telescope with a concave mirror behind the thermo-junction, and Féry has just designed such an instrument with which temperatures nearly as low as 600° C. may be reached.

CHAPTER IX.

OPTICAL PYROMETER.

Principle.—Instead of using the totality of the radiant energy as in the methods described in the preceding chapter, use is made of the luminous radiations only. This utilization may be effected in many different ways, which give methods of unequal precision and varying in facility of manipulation.

Before beginning their study, it is well to recall certain properties of radiations.

Kirchoff's Law.—An incandescent body emits radiations of different wave lengths. For a given wave length and a given temperature the intensity of this emitted radiation is not the same for different bodies: this is expressed by saying that they have for this radiation different *emissive powers*. Similarly, a body which receives radiations of a given wave length absorbs a part of them and sends back another part by diffusion or reflection; a certain quantity may also traverse the body. The *diffusing*, *reflecting*, or *transmitting* power at a given temperature, for a given wave length, varies from one body to another. The *emissive power and the diffusive power* (in the case of an opaque and non-reflecting body) *vary always inversely, resting complementary to each other.*

Substances of great emissive power, as lampblack, have a small diffusive power; substances of small emissive

power, as polished silver, magnesia, have a very great diffusing or reflecting power.

If we take as the measure of the emissive power the ratio of the intensity of the radiation of the body considered to that of a black body (p. 173) at the same temperature, and as measure of the diffusive power the ratio of the intensity of the radiation diffused to the incident radiation, the sum of these two quantities is equal to unity.

The emissive power of a body varies from one radiation to another, and consequently also its diffusing and transmitting powers, since these two powers are complementary to each other. It follows that the relative proportions of the visible radiations received or given off by a body are not the same; so that different bodies, at the same temperature, appear to us to be differently colored.

At the same temperature, the color proper to a body, and its apparent color when it is lighted by white light, are complementary to each other. Yellow substances, as oxide of zinc heated, emit a greenish-blue light. At temperatures less than 2000° the red radiations predominate greatly and mask the inequalities of the radiations of other wave lengths. To render easily visible the colorations of radiating bodies it is necessary to compare them with those of a black body under the same temperature conditions. A hole pierced in the body, or a crack across the surface, gives a very good term of comparison to judge of this coloration.

The intensity of the radiations emitted by a black body increases always with the temperature, and the more rapidly as we approach the blue region of the spectrum; but on the other hand the radiations from the red end are the first to commence to have an intensity appreciable to vision, so that the color of bodies heated to higher and

higher temperatures starts with red, tending towards white passing through orange and yellow. White is, in fact, the color proper to bodies extremely hot, as is the sun.

Bodies not black have a law of increase different from that for black bodies, because the emissive power varies with the temperature. It increases unequally for the various radiations, so that the color of bodies, with respect to the color of a black body, changes with the temperature.

The following table gives for different colors the ratios of the values of emissive powers of some bodies to that of a black body. The red radiation was observed through a glass containing copper, the green by aid of a chromium copper glass, the blue through an ammoniacal solution of cupric hydrate. The substance covered the junction of a thermoelectric couple, and was cut by grooves; and it was the brightness of the bottom of these grooves which was compared to that of the surface.

		Red.	Green.	Blue.
Magnesia.....	{ at 1300°	0.10	0.15	0.20
	{ 1550	.30	.35	.40
Lime.....	{ 1200	.05	.10	.10
	{ 1700	.60	.40	.60
Oxide of chromium..	{ 1200	1.00	1.00	1.00
	{ 1700	1.00	.40	.30
Oxide of thorium ...	{ 1200	.50	.50	.70
	{ 1760	.60	.50	.35
Oxide of cerium.....	{ 1200	.80	1.00	1.00
	{ 1700	.90	.90	.85
Auer mixture.....	{ 1200	.25	.40	1.00
	{ 1700	.50	.80	1.00

The estimation of temperature, from measurements of luminous radiations, may, at least in theory, be made directly in three different ways, by utilizing:

The total intensity of the luminous radiation;

The intensity of a radiation of definite wave length;

The relative intensity of radiations of definite wave lengths.

In the chapter (VII) on the laws of radiation we have discussed the recent theoretical and experimental advances underlying these methods.

Measurement of the Total Intensity of Radiation.—The brightness of substances increases very rapidly with the temperature. One may with the unaided eye estimate comparatively this brightness, but this measurement is very uncertain, for lack of a constant standard of comparison. The sensitiveness of the eye varies, in fact, with the individual, with the light which the eye received immediately preceding, and with the attendant fatigue. Photometric processes, precise for comparison with a standard source, cannot be employed on account of the change of hue with the temperature.

The following method might be tried: trace on a white surface, diffusive or translucent marks, of definite intensity and dimensions, and seek what fraction of the light must be employed to render the marks invisible. The indications will be still quite variable and will depend upon the degree of the eye's fatigue.

We can then say that there actually exists no definite method based on the appreciation of the total intensity of luminous radiation for the estimation of temperatures.

Measurement of the Intensity of a Simple Radiation.—We may estimate the temperature of a body from the intensity of one of its radiations, provided that we know the emissive power of the body at that temperature and the law of variation of this radiation determined in terms of the air-thermometer.

The emissive power varies with the temperature, and generally is not known. It might seem that this would

be enough to reject this method and similar methods by radiation. But this is not so, for the following reasons:

1. At temperatures higher than the fusing-point of platinum there is no other pyrometric method at present applicable.
2. A great many bodies have a considerable emissive power, nearly unity, and particularly some bodies of industrial importance, as iron and coal.
3. The variation of radiation with temperature is sufficiently marked so that the errors committed in neglecting the emissive power are small. Thus at 1000° the red radiation emitted by carbon is quadrupled for an interval of 100° ; it is doubled at 1500° for the same temperature interval.

Then, except for some bodies exceptionally white, the emissive powers at high temperatures are superior to 0.5. By taking them equal to 0.75, the greatest error that will be made for the ordinary temperatures comprised between 1000° and 1500° will be from 25° to 50° .

Furthermore, in cases where the emissive power is unknown, an optical pyrometer will still give a consistent temperature scale for a given body, *i.e.*, in terms of black-body temperatures (p. 176).

Optical Pyrometer of Le Chatelier.—Ed. Becquerel had proposed in 1864 to refer the measurement of high temperatures to the measurement of the intensity of red radiations emitted by incandescent bodies; but this method had never been realized in a complete manner, and still less employed. Le Chatelier, taking up the question, devised an experimental arrangement suitable for such measurements, and he determined a *law of radiation* of substances in terms of the temperature.

Photometer.—For these measurements a photometric

apparatus is required which gives, not as do the ordinary photometers, a measurement of the total illumination pro-

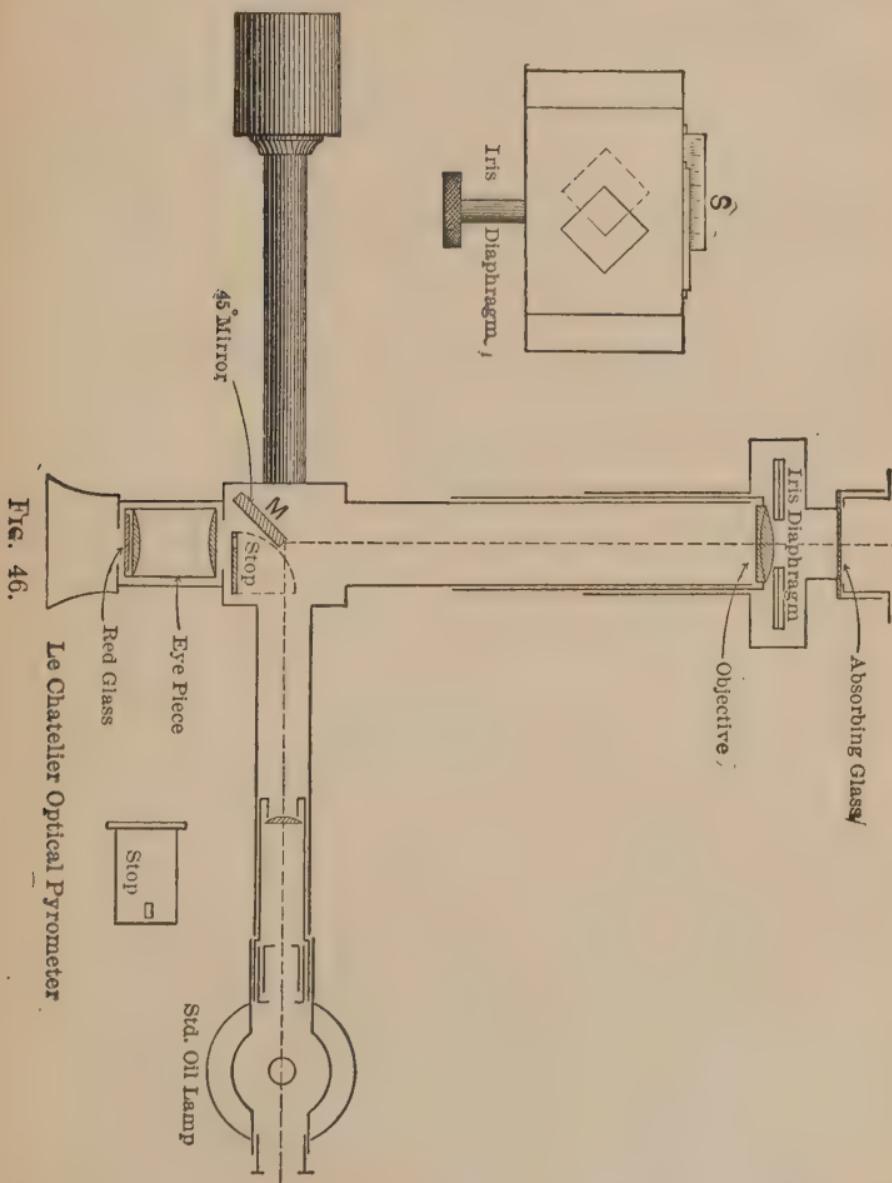


FIG. 46.

Le Chateller Optical Pyrometer.

duced by a source (illumination which varies with the dimensions of this source), but the intrinsic brightness of

each unit of surface. Use may be made of a photometer based on a principle due to Cornu.

The apparatus (Figs. 46 and 47) consists essentially of a telescope which carries a small comparison-lamp attached laterally. The image of the flame of this lamp is projected on a mirror M at 45° placed at the principal focus of the telescope. One adjusts for equality of intensity the images of the object that is viewed and of the comparison-flame, these images being side by side.

The telescope comprises an objective in front of which is placed a cat's-eye diaphragm which admits of varying the effective aperture of this objective, and, beyond, a stand destined to carry tinted absorbing-glasses.

At the focus of the objective is a mirror inclined at 45° which reflects the image of the lamp projected by an intermediary lens. An ocular, before which is placed in a set position a monochromatic glass, serves for observing the images of the flame and of the object.

To the lamp is fixed a rectangular diaphragm which stops the luminous rays not utilized and which carries a stand to receive tinted absorbing-glasses.

The edge of the mirror at 45° is in the plane of the image of the source studied, so that the reflected image and the direct image are side by side, separated only by the edge of the mirror. This mirror, according to a method devised by Cornu, is made of a plate of black glass cut with a diamond, which gives a very sharp edge.

In order to vary the relative intensities of the images, one thus employs simultaneously tinted glasses placed before one or the other of the two objectives, and the cat's-eye mentioned. A screw allows of varying the aperture of this cat's-eye, and a suitable scales indicates the dimensions of this opening.

It is very important that the tinted glasses have an

absorbing power as uniform as possible and do not possess absorption-bands. These conditions are fulfilled by certain smoked glasses of ancient make ($\text{CuO}, \text{Fe}_2\text{O}_3, \text{MnO}_2$); for the fabrication of these glasses use is now made of the oxides of nickel and cobalt, which give absorption-bands.

To determine the absorbing power of these glasses, a measurement is made with and without them; the ratio

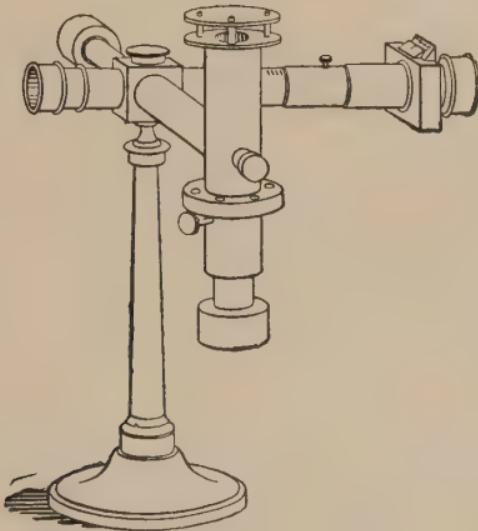


FIG. 47.

of the squares of the aperture of the cat's-eye gives the absorbing power.

For monochromatic screens one may use:

1. Red copper glass, which lets pass $\lambda=659,*$ about. This one is preferable, as it is more nearly monochromatic and because measurements at low temperatures may be made with it, the first radiations emitted being red.

* Red glasses furnished by the maker Pellin, Paris, have an equivalent wave length of about $\lambda=632$.

2. Green glass ($\lambda=546$, about). The observations are then easier than in the red for some eyes, but they can be commenced only at higher temperatures.

3. Ammoniacal solution of copper oxide ($\lambda=460$, about). The use of this last screen, which is far from monochromatic, is without interest; the eye is only slightly sensitive to the blue radiations, and these last become somewhat intense only at high temperatures.

Adjustment of the Apparatus.—There are in the apparatus two parts which require very careful adjustment for best results, and these parts should consequently be so made as to admit of the necessary manipulation to obtain the desired effect.

1. The luminous beam coming from the lamp and which is reflected by the mirror, and that which comes directly from the object viewed, should penetrate into the eye in their totality. This condition is fulfilled if the images of the two objectives given by the ocular are superposed.

This is verified by examining with a lens these two images which are formed slightly behind the collar of the ocular. It is evidently necessary, in order to see them, to illumine the two objectives, one with the lamp, the other with any source of light. If the superposition does not exist, it is established by trial by turning the screws which hold the mirror. If it is not too severely jarred, the apparatus should remain indefinitely in adjustment.

In order that a steady light may be had, certain precautions in the adjustment of the comparison-lamp are necessary. As far as possible, one should always employ the same gasolene. The flame should have a constant height, equal, for example, to the window of the rectangular diaphragm placed before the flame. Its image should be cut exactly in two by the edge of the mirror, a result

obtained by turning the lamp in its stand, which is eccentric (Fig. 48).

Finally, before taking an observation, one must wait some ten minutes for the lamp to come into heat equilibrium; then only does the flame possess a constant brightness.

Measurements.—In order to take an observation, a body selected as standard, as the flame of a stearine candle or the flame of a kerosene lamp, is examined; one observes:

1. n_0 , the number of absorbing-glasses;
2. d_0 , the aperture of the cat's-eye;
3. f_0 , the extension of the objective for focussing.

The same process is followed for the source to be studied, and the numbers n_1 , d_1 , f_1 are found.

k being the absorption coefficient of the tinted glasses, we have:

$$\frac{I}{1} = \left(\frac{1}{k}\right)^{(n_1 - n_0)} \cdot \left(\frac{d_0}{d_1}\right)^2 \cdot \left(\frac{f_1}{f_0}\right)^2.$$

For the glasses mentioned, the absorption coefficients are:

$$\begin{aligned} k &= 1/11, \text{ corresponding to } \lambda = 659; \\ k &= 1/7, \quad " \quad " \quad " \quad \lambda = 546; \\ k &= 1/10, \quad " \quad " \quad " \quad \lambda = 460. \end{aligned}$$

For very small objects which would have to be placed very near, a supplementary objective is put in front of the telescope; the object is placed in the principal focus of this

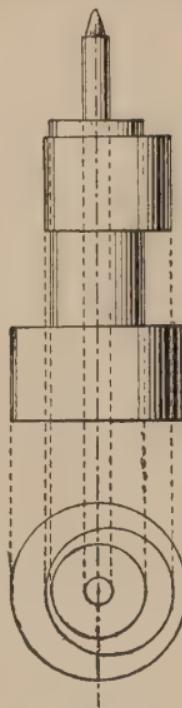


FIG. 48.

new lens, the objective of the apparatus being focussed for parallel rays. The absorptive power of this supplementary lens is reckoned as $1/10$.

Details of an Observation.—The first operation to make is the determination of the absorption coefficients of the absorbing-glasses. For that, one views an object of suitable brightness once with the tinted glass before the cat's-eye and then without this glass. Let N be the aperture of the cat's-eye without tinted glass, and N' the aperture with such a glass. The coefficient k of absorption is

$$k = \left(\frac{N'}{N}\right)^2.$$

The following observations furnish data for the determination of the absorbing powers of different glasses employed in the course of studies relative to the radiations from incandescent mantles.

Emissive Power.—Before being able to establish the relation which exists between the intensity of radiation of incandescent bodies and their temperature, it is necessary to know the emissive powers of these bodies. For this measurement use is made of the principle stated above, that the interior of fissures in bodies may be considered as enclosed in an envelope at uniform temperature. The emissive power is thus, at the temperature considered, equal to the ratio of the luminous intensity of the surface to that of the bottom of deep fissures, with the condition, evidently, that the aperture of the fissures be sufficiently small.

The body to be studied was placed in the state of a paste, as dry as possible, on the end of a couple previously flattened so as to take the form of a disk of 2 or 3 mm. diameter. The drying was very slow, so as not to have

ABSORBING-GLASS PLACED BEFORE THE SOURCE TO BE STUDIED.

Temperature.	Aperture of Cat's-eye.		
	Red.	Green.	Blue.
1270° (+1 glass).....	19.5	21.2	35
1270 (no glass).....	5.5	7.9	11.1
	$k_r = 12.5$	$k_g = 7.2$	$k_b = 9.9$

ABSORBING-GLASS PLACED BEFORE THE STANDARD LAMP.

1170° (-1 glass).....	2.9	5.95	10.2
1170 (no glass).....	9.4	16.1	31.5
	$k_r = 10.5$	$k_g = 7.3$	$k_b = 9.5$

any swelling of the mass, and one obtained in this way a coating possessing fissures; the conditions described above are then satisfied. The end of the couple thus prepared is heated either in a Bunsen flame or a blast-lamp, and the temperature of the junction is noted, while, simultaneously, readings are taken with the optical pyrometer. In order to obtain a temperature as constant as possible, it is necessary to guard against currents of air and use a flame of small size.

Here are some results obtained:

I. COUPLE COVERED WITH A MIXTURE CONTAINING 99 PARTS OF THORIUM AND 1 OF CERIUM.

Temperatures.	Red.		Green.		Blue.	
	(1)	(2)	(1)	(2)	(1)	(2)
950° (-1 glass).....	16.0	...	21.0	14.0	23.0	
1170	15.5	9.0	11.0	9.0	12.0	12.0
1375	7.0	3.0	4.5	3.2	3.5	3.5
1525	3.2	2.0	2.0	2.0	1.9	1.9
1650 (+1 glass).....	8.3	6.0	5.0	4.0	

II. MAGNESIA.

1340° (-1 glass)	12.2	4.0	18.5	6.7	19.0	9.0
1460 (-1 glass)	4.9	2.5	8.2	3.1	7.7	4.1
1540 (-1 glass)	2.4	1.3	3.1	1.8	3.2	2.1

The numbers give the divisions of the cat's-eye; those of column (1) refer to the surface, and those of column (2) to the bottom of the fissures. The indications (-1 glass) and ($+1$ glass) mean that the absorbing-glass is placed either before the standard lamp or before the source studied. A more exact determination of the above quantities might be made with the electrically treated black body (p. 174).

Measurements of Intensity.—The following table gives an idea of the order of magnitude of the intensities of different luminous sources, the measurements of brightness being made in the red. Unity is the brightness of the axial portion of stearine-candle flame.

Carbon beginning to glow (600°).....	0.0001
Silver melting (950°).....	0.015
Stearine candle,	
Gas-flame,	
Acetate of amy1 lamp,	1.0
Pigeon-lamp, with mineral oil.....	1.1
Argand burner, with chimney.....	1.9
Auer burner.....	2.05
Fe ₃ O melting (1350°).....	2.25
Palladium melting.....	4.8
Platinum melting.....	15.0
Incandescent lamp.....	40
Crater of electric arc.....	10,000
Sun at midday.....	90,000

Graduation.—Le Chatelier made a first graduation of his optical pyrometer by measuring the brightness of iron

oxide heated on the junction of a thermoelectric couple, and admitting that, for the red, the emissive power of this substance is equal to unity.* He found a law of variation of the intensity of the red radiations as function of the temperature, which is well represented by the formula

$$I = 10^{6.7} \cdot T^{-\frac{3210}{T}},$$

in which unit intensity corresponds to the most brilliant axial region of the flame of a candle. (T is absolute temperature.)

The table below gives, for intervals of 100° , the intensities of red radiations emitted by bodies of an emissive power equal to unity. These numbers were calculated by means of the interpolation formula given above.

Intensities.	Temperatures.	Intensities.	Temperatures.
0.00008 . . .	600°	39	1800°
.00073	700	60	1900
.0046.	800	93	2000
.020.	900	1,800	3000
.078.	1000	9,700	4000
.24.	1100	28,000	5000
.64.	1200	56,000	6000
1.63.	1300	100,000	7000
3.35.	1400	150,000	8000
6.7.	1500	224,000	9000
12.9.	1600	305,000	10000
22.4.	1700		

These results are represented graphically in Fig. 49.

After having determined the value of the diaphragm

* It has since been shown that the emissive power of iron oxide is less than unity (see p. 178), but this fact does not materially affect the applicability of Le Chatelier's formula as used.

opening d_0 , which gives equality of brightness of the standard candle with that of the comparison-lamp, and the absorbing power k of the tinted glasses, one may, as was said before, prepare a table which gives directly the temperature corresponding to each aperture of the cat's-eye.

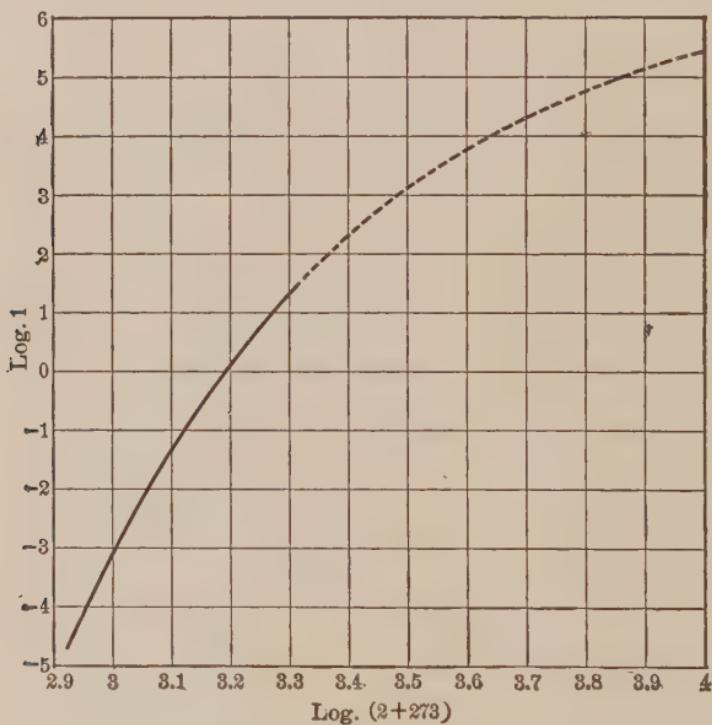


FIG. 49.

With an apparatus for which

$$d_0 = 5.2, \quad k = \frac{1}{11},$$

the following table is obtained, in which the plus sign refers to tinted glasses placed before the objective, and the minus sign to those before the comparison-lamp.

This graduation applies to all bodies placed in an enclosure at the same temperature, in the interior of fur-

naces for example, and to black bodies whatever the temperature surrounding them; for example, it applies very closely for a piece of red-hot iron exposed to the free air. For bodies whose emissive power is inferior to unity, as platinum, magnesia, lime, it is necessary, when they are exposed to the air and not surrounded by an enclosure at the same temperature, to make a special graduation.

Temperatures.	Aperture of the Cat's-eye.				
	-2 Glasses.	-1 Glass.	0 Glass.	+1 Glass.	+2 Glasses.
700°	17.3
800	6.9	23.0
900	11.0
1000	5.6	18.6
1100	10.5
1200	6.5
1300	4.0	13.6
1400	9.4
1500	6.6
1600	4.8
1700	3.6	12.0
1800	9.1
1900	7.3
2000	5.9

Le Chatelier and Boudouard have made a series of measurements on radiations of different wave lengths. The junction of a thermoelectric couple was placed in a small platinum tube, to realize approximately an enclosed space. By taking as unity the brightness of melting platinum, the results obtained are the following for the red, green, and blue radiations:

<i>t</i>	Log (<i>t</i> +273)	<i>I_r</i>	Log <i>I_r</i>	<i>I_v</i>	Log <i>I_v</i>	<i>I_b</i>	Log <i>I_b</i>
900°	3.0707	0.0009	4.95	0.00018	4.25	0.00002	5.3
1180	3.161	.0024	3.88	.0087	3.94	.0015	3.17
1275	3.190	.075	2.78	.037	2.57	.013	2.11
1430	3.230	.23	1.36	.16	1.67	.058	2.76
1565	3.265	.72	1.86	.47	1.20	.24	1.38
1715	3.300	1.69	0.23	1.45	0.16	.9	0.95

Evaluation of Temperatures.—Finally, Le Chatelier has used his optical pyrometer to determine the very highest temperatures realized in some of the most important phenomena in nature and in the industries. These results, quite different from previous determinations, were at first regarded with considerable reserve; they are admitted to-day as exact, at least within the limits of precision. Here are some of the figures obtained:

Siemens-Martin furnace	1490° to 1580° C.
Furnace of glass-works	1375 to 1400
Furnace for hard porcelain	1370
" " new porcelain	1250
Incandescent lamp	1800
Arc lamp	4100
Sun	7600

This determination of the temperature of the sun, generally believed to be low at the time it was found, has been confirmed by the more recent experiments of Wilson and Gray (p. 194) by a totally different method. Later determinations of the sun's temperature, using the recently established laws of radiation (Chapter VII), give values between 5500° and 6500°.

A series of measurements were made with the same apparatus in iron-works. Here are some results:

BLAST-FURNACE SMELTING GRAY PIG.

Opening before the tuyère	1930° C.
Tapping the pig iron, beginning	1400
" " " " " end	1520

BESSEMER CONVERTER.

Pouring the slag	1580°
" " steel into the ladle	1640
" " " " " moulds	1580
Reheating of the ingot	1200
End of the hammering	1080

SIEMENS-MARTIN FURNACE.

Flow of the steel into the ladle, beginning.....	1580°
“ “ “ “ “ “ end.....	1420
“ into the moulds.....	1490

Calibration in Terms of Wien's Law.—As approximately monochromatic radiation is used, the Le Chatelier optical pyrometer may be calibrated in terms of Wien's law III (p. 183) by sighting upon a black body (p. 173) whose temperature is given by means of a thermocouple. For this purpose Wien's law may be written:

$$\log J = K_1 + K_2 \frac{1}{T},$$

where J is the intensity of light, in terms of the centre of the Hefner flame for example, and T is the absolute temperature. This method of graduation has the advantage that only two points are required to completely calibrate the instrument, for the relation between $\log J$ and $\frac{1}{T}$ is linear, so that these quantities being plotted give a straight line which may evidently be extended to lower and higher temperatures, since Wien's law has been shown (p. 183) to hold over the widest temperature interval measurable, provided the light used is monochromatic and the bodies observed approximate blackness and are not luminescent, that is, their light not produced by chemical or electrical excitation.

Precision and Sources of Error.—We shall give in some detail a discussion of the factors which in the use of the Le Chatelier optical pyrometer may influence the photometric settings and so affect the accuracy of temperature determinations, as results of such a discussion are illustrative of what may be expected from optical pyrometers in general. The results are taken from those of Waidner

and Burgess, who have made an experimental comparison of all the available optical pyrometers.

The sources of error of this instrument may be those due to the standard Hefner amyl-acetate or other standard, the oil comparison-lamp, the focussing system, the nature of the red glass used, and the coefficients of absorption of the glasses used. The first of these affects only comparative results with different instruments, while the others, if they exist, may be of considerable importance in work with a single instrument. We shall consider them in the order named.

As only the central portion of the amyl-acetate flame is used, variations in height and fluctuations in total intensity due to various causes such as moisture and carbonic acid in the atmosphere and changes due to differing samples of acetate become almost, if not quite, insignificant in this method of comparison; so that when using only a small central area of the amyl-acetate flame, it is a very perfectly reproducible standard under the most varying conditions of burning. Again, the effects of any slight fluctuations in light-intensity are further greatly reduced when transformed into temperature changes as has been shown (p. 171). Thus, the effect of varying the height of the Hefner flame by one millimeter, which amounts to ten per cent of the total intensity when the whole flame is used, causes a change of less than one per cent in the intensity of light from the central area, which is equivalent to less than $0^{\circ}.5$ C. change in temperature at 1000° C.

Although used intermittently as above indicated, the Hefner serves well enough as an ultimate standard by means of which the indications of all photometer-pyrometers may be reduced to a common basis, yet the Hefner is not suited for use as comparison-lamp in the pyrometer itself, as has been previously stated.

In a study of the constancy of the comparison-lamp the following arrangement was adopted: In order to obtain a perfectly constant source of light with which to compare the flame, a 32 c.p. incandescent electric lamp was placed in a fixed position before the objective of the pyrometer and a glass diffusing screen inserted before the objective. The voltage across the lamp terminals was kept rigorously constant thus giving an arbitrary but invariable standard of illumination.

The concordance of results obtained by different observers setting the gasoline flame and observing is shown below:

WITHOUT ABSORPTION-GLASS.

Observer.....	1	2	3	4
Cat's-eye scale readings...	7.4	7.8	7.6	7.3
	7.4	7.9	7.8	7.0
	7.2	7.7	7.6	8.0
	7.8	7.8	7.7	7.1
	7.7	7.7	7.8	8.3
	7.8	7.7	7.4	8.0
Means.....	7.55	7.73	7.65	7.60

Observers Nos. 2 and 4 had no experience in the use of the instrument.

WITH ABSORPTION-GLASS.

Observer.....	1	3
Cat's-eye scale readings...	25.7	25.8
	24.0	24.8
	23.6	26.0
	24.1	25.8
	25.4	24.8
	24.8	24.9
	24.8	25.3
Means.....	24.63	25.34

Here the greatest variation corresponds to less than three degrees in temperature at 1000° C.

To control accurately the flame height in the gasoline lamp, a sight was inserted consisting of a horizontal scratch 2 mm. above the window before the flame, and a very fine platinum wire in the same horizontal plane but in a collar behind the flame. With this improvement an observer can set and control the flame-height to 0.2 mm. Such provision, however, is not necessary except in the most refined work, for experiment showed that for most purposes changes of over 2 mm. may be made in the flame height with unimportant changes resulting in the temperature estimation.

Considering the time-effect of burning upon the flame-height and intensity due to local heating and change of depth of oil, it was found that the flame ceases creeping up after ten minutes and will then remain at constant height to within 0.5 mm. until the oil is used up, in three hours, and during all this period the brightness of the flame does not change by an amount corresponding to more than 5° in temperature.

It might be expected that oils of different grades would give widely differing results, but an examination of this possible source of error showed that different samples of gasoline and gasolenes mixed with several per cent of a heavy kerosene gave identical results. This is of great importance in the practical use of the instrument as it shows that a calibration made with a given sample of gasoline remains good for any other gasoline.

From the above it is clear that variations in brightness of the comparison-flame due to all possible causes need not produce errors in temperature measurement of over 5° C. at 1000° C., that is within the experimental limits of making the photometric setting.

Considering now the sources of error due to focussing and sighting upon the object whose temperature is sought, it is first to be noticed that there is a minimum distance from the object at which the pyrometer can be focussed, this distance being somewhat over a meter, depending, of course, upon the focal length of the objective and length of draw-tube. There is also a minimum area which can be sighted upon and give an image of sufficient size to completely cover the desired photometric field; this minimum size of object is about 6 mm. on a side when the instrument is at its least distance; for greater distances a larger area must be viewed.

The draw-tube can easily be set to 2 mm. when focussing, and as the image is over 20 cm. from the objective in all cases, the resulting error in intensity due to focussing is not greater than 2 per cent. This corresponds to 1° C. in temperature, showing that an error of even 5 mm. in focussing the draw-tube will not produce an appreciable error in temperature estimation.

Often, in use, the distance of the instrument from the objects studied needs to be changed considerably, and in rapid work it is not always convenient to refocus; a change in this distance of a fourth of its value, *i.e.*, from 120 cm. to 150 cm., will produce an apparent change in intensity of only 9 per cent, or about 5° C. in temperature. That these errors of focussing are so small when interpreted into temperatures, showing that no unusual precautions are needed, is evidently of great convenience in the use of the instrument.

The non-monochromatism of the red glass in the eyepiece produces no considerable error in temperature-measurement up to 1600° C., although if this glass is not very nearly monochromatic the differences in hue in the two adjacent photometric fields—from the compari-

son-lamp and other sources—are very troublesome, and the strain on the eye in matching them is considerable. For the best work at high temperatures a better glass than is usually furnished with the instrument must be used.

There remains to be considered the error introduced due to uncertainty in the knowledge of the coefficient of absorption of the absorbing-glasses. If an observation (N') is taken with, and then one (N) without, an absorption-glass, we have

$$k = \left(\frac{N'}{N} \right)^2,$$

so that the accuracy in determining k depends directly upon the precision of setting and reading the cat's-eye opening. Errors of over 5° at 1000° C. can hardly occur from this cause, although the determination of k is the most difficult and uncertain of all the operations in optical pyrometry.

Modifications of the Le Chatelier Pyrometer.—For use in technical works and other places where there are sure to be strong drafts of air causing unsteadiness of the flame of the oil comparison-lamp, the Le Chatelier pyrometer might be improved by the substitution of an electric incandescent lamp of low voltage (six) placed before a uniformly ground diffusing-glass screen, which, illuminated by the incandescent lamp, becomes the constant comparison source. The electric lamp may be mounted in a vertical arm which serves at the same time as a handle, and then the instrument becomes as portable as an opera-glass. The reliability of such a method of producing a comparison-light of invariable intensity will be discussed when describing the Wanner instrument. Other modifications will be discussed under the Féry and Wanner pyrometers.

Féry Absorption-pyrometer.—This is identical with Le Chatelier's instrument, except that a pair of absorbing-glass wedges p , p' replaces the iris diaphragm, and the 45°

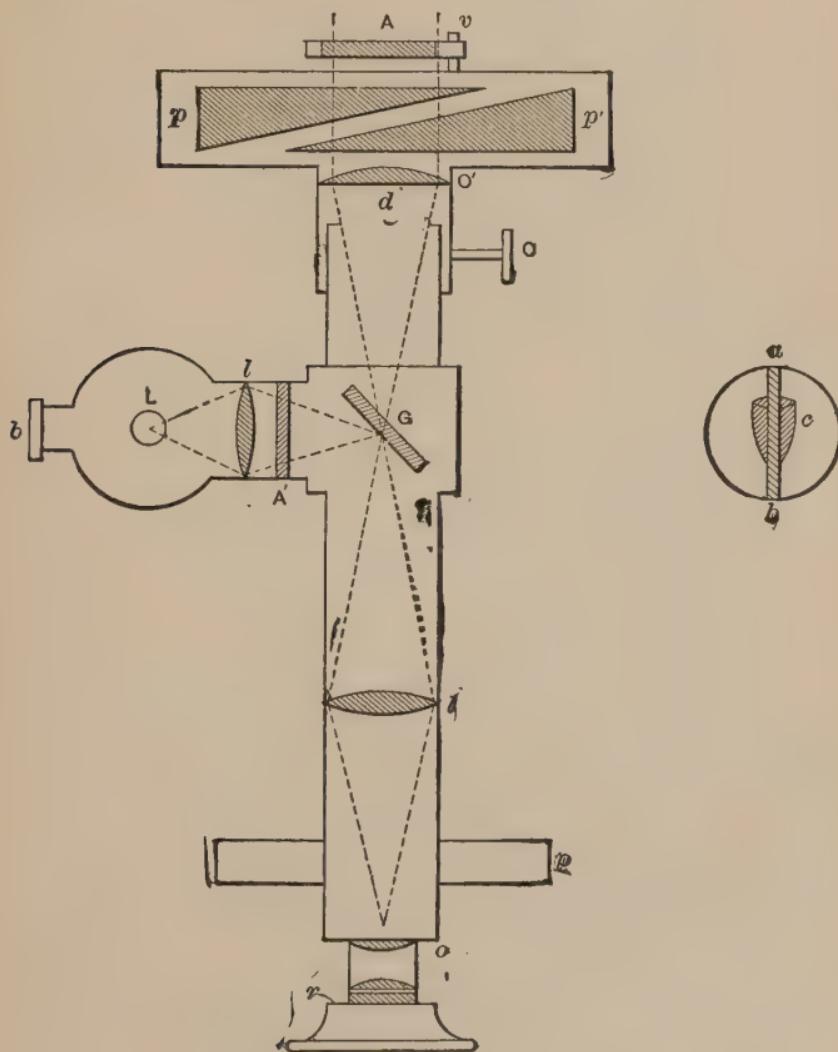


FIG. 50.

mirror G , with parallel faces, is silvered over a narrow vertical strip, giving a photometric field of form shown

at ab , when looking at a hot crucible. The instrument has a fixed angular aperture, so that no correction has to be made for focussing or for varying distance from furnace. The comparison-light L plays the same rôle as in Le Chatelier's pyrometer, and the range of the instrument may be similarly extended by the use of auxiliary absorbing-glasses. Féry has in addition made his instrument movable about a horizontal axis, which is a convenience.

The calibration is equally simple. If x is the thickness of the wedges, read off on a scale, when the light from the comparison-lamp and furnace is of the same brightness, then the relation between brightness I and thickness of wedge is

$$I = ce^{kx},$$

where k is the coefficient of absorption of the glass of the wedges for the red light used and c is a constant.

But by Wien's law III (p. 183), assuming it to apply here,

$$I = Ae^{-\frac{B}{T}},$$

or combining these two equations we have

$$ce^{kx} = Ae^{-\frac{B}{T}},$$

whence

$$kx + C = -\frac{B}{T}.$$

Thus it follows that the thickness of the wedge is inversely proportional to the absolute temperature, so that the calibration may be effected by finding the thickness of wedge for two temperatures only and plotting a straight line and constructing a table giving I and T respectively in terms of x .

It is questionable if there is any gain in substituting the wedge for the cat's-eye in the desire to extend the range over which the instrument may be used without employing the auxiliary absorbing-glasses, for thereby the sensibility is somewhat reduced, and more important still, the wedge instrument cannot be used at such low temperatures as the original Le Chatelier form, nor is there any gain in simplicity of calibration and ease of manipulation. The shape of the photometric field, the use of an aperture of constant angle, and making the instrument movable about a horizontal axis, however, are improvements which may be applied with advantage to the Le Chatelier instrument.

Wanner Pyrometer. — *Description and Calibration.* — Wanner, making use of the polarizing principle discarded by Le Chatelier, has brought out a photometer-pyrometer which is a modification, suited to temperature-measurements, of König's spectrophotometer.*

The comparison-light is a six-volt incandescent lamp, illuminating a glass-matt surface; monochromatic red light is produced by means of a direct-vision spectroscope and screen cutting out all but a narrow band in the red, and the photometric comparison is made by adjusting to equal brightness both halves of the photometric field by means of a polarizing arrangement.

The slit S_1 is illuminated by light from the comparison source reaching S_1 after diffuse reflection from a right-angled prism placed before S_1 . Light from the object whose temperature is sought enters the slit S_2 . The two beams are rendered parallel by the lens L_1 , and each dispersed into a continuous spectrum by the direct-vision prism P . Each of these beams is next separated by a

* König, Wied. Ann., 53, p. 785, 1894.

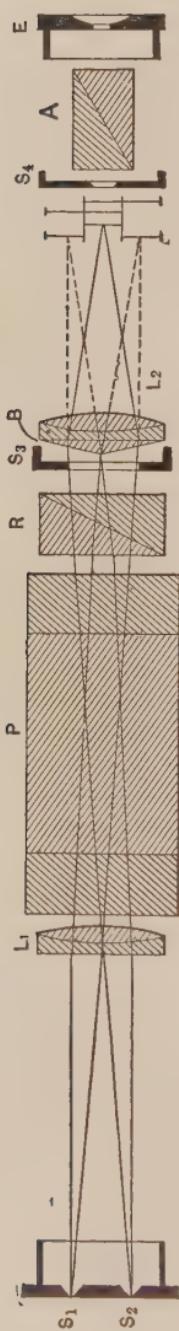


FIG. 51.

Rochon prism R into two beams, polarized in planes at right angles. Considering only the red light, there would now be four images formed by the lens L_2 , and distributed about the slit S_4 . In order to bring two red images oppositely polarized exactly before this slit, a bi-prism B is interposed whose angle is such as to effect this for two images only, at the same time increasing the number of images to eight. There is now in the field of view before the Nicol analyzer, A , two contiguous red fields composed of light oppositely polarized, the light of one coming from S_1 alone, and of the other from S_2 alone. All the other images are cut off from the slit S_4 . If the analyzer is at an angle of 45° with the plane of polarization of each beam, and if the illumination of S_1 and S_2 is of the same brightness, the eye will see a single red field of uniform brightness. If one slit receives more light than the other, one-half of the field will brighten, and the two may be brought to equality again by turning the analyzer carrying a graduated scale, which may be calibrated in terms of temperature.

If the analyzer is turned through an angle ϕ to bring the two halves of the field to the same brightness, the relation between the two intensities from S_1 and S_2 is

$$\frac{J_1}{J_2} = \tan^2 \phi. \quad \dots \dots \dots \quad (a)$$

Since monochromatic light is used, and the comparison-beam and that from the object examined undergo the same optical changes, Wien's law III may form the basis of the calibration.

If J_0 is the intensity of the light from the standard and J that from the object whose temperature is sought, Wien's law III gives

$$\log_{10} \frac{J_0}{J} = \frac{C \log e}{\lambda} \left(\frac{1}{T} - \frac{1}{T_0} \right). \quad \dots \dots \quad (b)$$

Since the constant $C = 14,500$ for a black body and $\lambda = 0.656\mu$ as the instrument is usually constructed, a knowledge of the apparent black-body temperature of the standard source, together with the reading of the analyzer-scale at the normal point when $J = J_0$, for such an instrument, is all the data required for its calibration, as any temperature may then be calculated by means of equations (a) and (b) in terms of the scale-readings. This instrument may also of course be empirically calibrated against a thermocouple using a black body to sight upon.

It is evidently necessary to be able to always reproduce exactly the standard intensity J_0 . Now the brightness of an electric lamp will vary with the current through it, so it is necessary to check frequently the constancy of illumination of the slit S_1 against a standard source of light. An amyl-acetate lamp and a ground-glass diffusing-screen can be placed before the slit S_2 , thus furnishing the standard light required. The analyzer is then set at the previously determined normal point and the distance of the electric lamp from S_1 adjusted or the

current through the lamp changed by a rheostat, until the two fields appear of the same brightness.

Sources of Error.—A study of a Wanner instrument by Waidner and Burgess has led them to the following

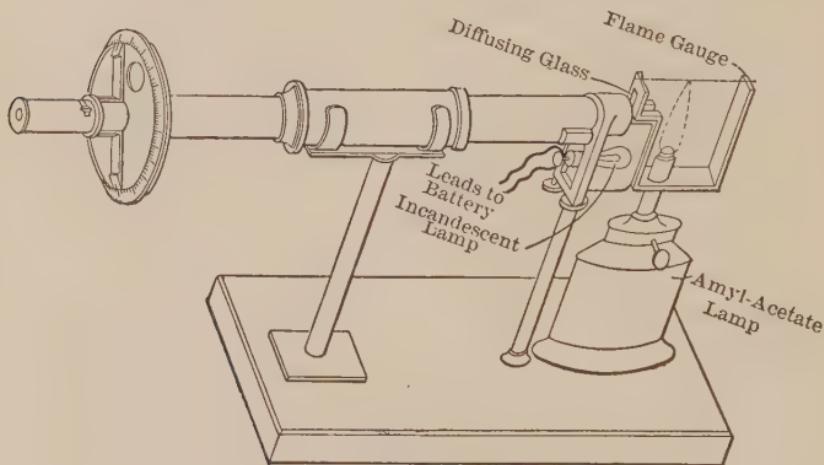


FIG. 52.

conclusions. The sensibility of this pyrometer varies with change in the angle, and is so adjusted as to be the greatest between 1000° and 1500° C. and is about as follows:

0.1 scale div.	1° C. at 1000° C.
0.1 scale div.	2° C. at 1500° C.
0.1 scale div.	7° C. at 1800° C.

The reproducibility of the brightness of the amyl-acetate flame as viewed through the ground-glass diffusing-screen is a measure of the ability of the instrument to repeat its indications. It is very important that this diffusing-screen be always placed in exactly the same position relative to the flame and slit S_2 , and further that it be free from dust and finger-marks. These requirements can only be satisfactorily met by protecting this

screen by a cover-glass and providing an adjustment for setting it exactly in place between the flame and slit.

The constancy of the amyl-acetate flame as used with this pyrometer under ordinary conditions of burning is illustrated by the following set of observations, during which the current through the electric comparison-lamp was kept rigorously constant by means of a milliammeter and rheostat:

Reading of Instrument.	Deviations.
39.9	-0.28
39.9	-0.28
40.1	-0.48
39.9	-0.28
39.1	+0.52
39.2	+0.42
39.8	-0.18
39.0	+0.62
<hr/> 39.6	<hr/> 0.38

This shows that the flame can be relied upon to give an intensity of illumination whose constancy expressed in terms of temperature is 0.5 per cent. Variations in height of the flame, if they do not exceed 2-3 mm., together with fluctuations in atmospheric conditions, will not produce errors in temperature estimation exceeding 1 per cent.

The uncertainty of setting the nicol, due to lack of sensitiveness of the eye to exactly match the two halves of the photometric field, is also about 1 per cent, or slightly better with practice.

The adjustment of the electric lamp to standard intensity at the point on the scale chosen as normal point can be made, when proper care is taken regarding the diffusing-screen, to 1 per cent expressed in temperature change.

This source of error does not effect relative results in any one series for one setting to the normal point.

The most serious source of error, except when special precautions are taken, is the variation in brightness of the electric comparison-lamp due to variation in the current furnished by the three-cell storage-battery.

With the 10-ampere-hour battery furnished with the Wanner instrument, after making circuit the electro-motive force drops by about 2 per cent in two minutes and then falls off slowly, but nearly recovers the original voltage after remaining on open circuit even for a very short time. When the battery is in good condition the variation in three hours at normal discharge (0.075 ampere) is about 0.08 volt, and somewhat less for the current (0.55 ampere) taken by the lamp; with the battery in poor condition these changes are much accentuated.

The following table illustrates the effect of slight variations in current through the lamp on apparent temperature of the amyl-acetate flame, for the small battery of 10 ampere-hours furnished with the instrument. The apparent change in temperature is calculated from the current change:

SMALL BATTERY.

Time, Minutes.	Wanner Scale.	Current.	Per Cent Change in Current.	Apparent Change in Temp.
15	31.2	0.5645		
20	31.8	0.5640	0.1	1° C.
27	32.7	0.5550	1.7	10
37	34.6	0.5400	4.3	25
36	Disconnected battery two minutes.			
40	32.5	0.5610	0.6	3
42	31.7	0.5570	1.5	7
45	32.5	0.5560	2.5	15
47	33.1	0.5505	4.1	24

A battery of 75 ampère-hours gave similar results.

The above results give abundant evidence of the need of maintaining the current through the lamp quite constant in work of precision. A series of experiments has shown that in the range 1000°–1500° C. one division on the Wanner scale corresponds to about 0.009 ampere, or 1° C. apparent change in temperature is produced by a fluctuation of 0.0012 ampere through the lamp; hence to obtain a precision of 5° the current must be kept constant to 0.01 of its value. The above table shows that this is by no means effected by using the battery without regulating the current, for even with the battery in the best condition the current increases by 2 per cent in the first eight or nine minutes of discharge and then falls off 1 per cent in the next twenty minutes. The temperature coefficient of the battery would produce only insignificant changes. The table shows further that breaking the circuit and then making it again may cause an apparent temperature change of over 20° C. For work of precision, therefore, it is essential to keep the current constant by means of a milliammeter and rheostat, otherwise uncertainties of over 25° C. will occur in the temperature measurements. These will increase with the battery in poor condition.

Range and Limitations.—The above description of the Wanner pyrometer has shown the great loss of light due to the optical system employed. This prevents measuring temperatures below about 900° C. (1650° F.) with this instrument. There is no method of sighting this pyrometer exactly upon the spot desired, except by trial, as no image of the object examined is formed in the eye-piece, but this inconvenience is in part compensated by not having to focus with varying distance from the object.

There is another limitation which may in certain cases become a serious source of error;—light from incandes-

cent surfaces is in general polarized and, as the Wanner instrument is a polarizing pyrometer, care must be taken to eliminate this source of error when it exists.

If an incandescent object is viewed normally the amount of polarized light is very small, but, as the angle of incidence increases, the proportion of light polarized becomes greater and greater. Besides varying with the angle of incidence, the amount of polarized light emitted varies widely with different substances, being greatest for polished platinum and very much less for iron, glass, etc. In some measurements made with the Wanner pyrometer on the temperature of an incandescent platinum strip in the neighborhood of 1350° C., Waidner and Burgess have found a maximum difference in the readings of 90° C. for positions of the instrument at right angles to one another in azimuth and for an angle of incidence of 70° with the normal to the surface. This introduces, under these conditions, the possibility of an error of 45° C. in the temperature-measurement. This source of error can be eliminated by taking the mean of four readings for azimuths 90° apart. The magnitude of the error arising from this cause is entirely negligible for all practical purposes for many substances, such as iron, porcelain, etc.

A review of the sources of error and limitations of the Wanner pyrometer shows that they may exert a relatively great effect on the temperature-measurements, and it was, therefore, thought worth while to emphasize them, but on the other hand they may all be practically eliminated with reasonable care, and the instrument then becomes one of great precision and convenience.

Holborn and Kurlbaum, and Morse, Pyrometers.—If a sufficient current is sent through the filament of an electric lamp the filament glows red at first, and as the current is increased, the filament, getting hotter and

hotter, becomes orange, yellow, and white, just as any progressively heated body. If now this filament is interposed between the eye and an incandescent object, the current through the lamp may be adjusted until a portion of the filament is of the same color and brightness as the object. When this occurs this part of the filament becomes invisible against the bright background, and the current then becomes a measure of the temperature as given either by a thermocouple or in terms of the intensity of illumination.

Holborn and Kurlbaum Form.—A small four-volt electric incandescent lamp L with a horseshoe filament is mounted in the focal plane of the objective and of the eye-piece of a telescope provided with suitable stops D , D , D , and a focussing screw S for the objective. The lamp circuit is completed through a two-cell storage battery B , a rheostat, and a milliammeter.

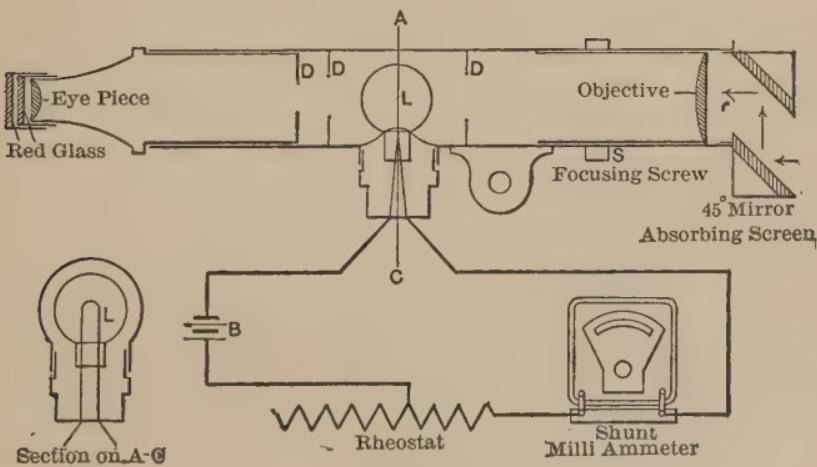


FIG. 53.

The determination of a temperature consists in focusing the instrument upon the incandescent object, thus bringing its image into the plane AC , and adjusting the

current by means of the rheostat until the tip of the lamp filament disappears against the bright background, when a previous calibration of current, in terms of temperature for the particular lamp used, gives the temperature by reading the milliammeter.

As the temperature of the filament increases, the effect of irradiation or too great brightness becomes blinding, and the photometric comparison is then rendered possible at these temperatures by the introduction of one or more monochromatic red glasses before the eye-piece, giving as well all the advantages of photometry of a single color. Below 800° C. the measurements are more easily made without any red glass, as the filament itself is then red and the lowest temperatures are, of course, reached with the least interposition possible of absorbing media. The lower limit of the instrument is very nearly 600° C. Two red glasses are required for temperatures above 1200° C., and for very high temperatures it is necessary in order to avoid overheating the lamp filament by the current to put absorbing-glasses or a double-prism mirror (Fig. 53) before the objective, and they also, of course, require calibration. At very high temperatures, unless a strictly monochromatic glass is used, the pyrometry becomes difficult, the filament never disappearing completely.

The coefficient of absorption of the prism system or of an absorbing-glass may be calculated by making use of Wien's law (p. 183), supposing it to hold for the red glass used. If K is the reciprocal of the coefficient of absorption, T_1 , T_2 the apparent temperatures (absolute) given by the pyrometer, sighting first without and then with the absorbing medium, then Wien's law III gives:

$$\log_{10} K = \log \frac{J_1}{J_2} = \frac{C \log e}{\lambda} \left(\frac{1}{T_2} - \frac{1}{T_1} \right),$$

where $C = 14500$ for a black body and λ is the wave length for the colored glass used. For very high temperatures, although this formula will give a consistent scale when K has been determined, yet the values obtained are in error by amounts depending upon the monochromatism of the red glass used and the departure of the source from a black body.

The eye is particularly sensitive in recognizing equality of brightness of two surfaces, one in front of the other, and this pyrometer, therefore, provides a very delicate means of judging temperatures, since the light-intensity, as has been shown (p. 171), varies so much faster than does the temperature.

The precision attainable with this pyrometer is illustrated by the following series of observations which are indicative of the ordinary performance of the instrument:

Temp. from H. & K. Pyrometer.	Temp. from Thermocouple.	Temp. from H. & K. Pyrometer.	Temp. from Thermocouple.
1347	1347° C.	632	634° C.
1351	1347	634	633
1343	1343	633	633
1333	1342	633	632
1342	1342		

Different observers do not differ by any appreciable amount in their readings, and at low temperatures the same values are obtained whether a red glass is used or not.

For the calibration of the instrument, it is necessary to find empirically the relation between the current through the lamp and the temperatures for a number of temperatures, and then interpolate either analytically, or, better,

graphically. The calibration will evidently be an independent one for each lamp used.

The relation between current and temperature is sufficiently well expressed by a quadratic formula of the form

$$C = a + bt + ct^2.$$

That this formula gives satisfactory results is shown by observations of Holborn and Kurlbaum for a lamp satisfying the equation

$$C10^3 = 170.0 + 0.1600t + 0.0001333t^2.$$

C amp	<i>t</i> obs.	<i>t</i> calc.	<i>Δt.</i>
340	686	679	-7° C.
375	778	778	0
402	844	850	+6
477	1026	1032	+6
552	1196	1196	0
631	1354	1354	0
712	1504	1504	0

The question whether or not the temperatures indicated by the lamp will repeat themselves for continued burning or aging is a vital one for the permanence of a calibration and hence for the practical usefulness of the pyrometer. Holborn and Kurlbaum as well as Waidner and Burgess have made a thorough study of this possible source of error.

Lamps which have not been aged or burned for some time at a temperature considerably above that at which they will ordinarily be used, undergo marked changes and are unreliable, but, if properly aged, they reach a steady condition, as indicated by the following table of results obtained by Holborn and Kurlbaum on these

lamps. The current is given in each case for a temperature of 1100° C.

AGING OF LAMPS.

Lamp Number.....	Current.		
	1	2	3
After 20 hours burning at 1900° C.....	0.608	0.592	0.589
" 5 " " " "613	.592	.592
" 5 " " " "621	.597	.597
" 5 " " " "622	.599	.600
" 20 " " " 1500° C.....	.622	.599	.601

If a lamp is not aged its indications may change by as much as 25° C. with time, but after twenty hours' heating at 1800° it will undergo no appreciable further changes over a period of time corresponding to many months if used in the shop, if not heated above 1500°. This state of permanence is sufficient to satisfy the most rigid requirements of practice.

Morse Form.—This instrument is based on exactly the same principle as the Holborn-Kurlbaum. It will only be necessary in describing it to point out the differences in construction from the German make.

Instead of a simple horseshoe filament, Morse uses a large spiral filament in the lamp so that in sighting upon an incandescent body it is necessary to choose some particular spot of the spiral and try to make that spot disappear. This is fatiguing, as the spiral covers a large area and is of just sufficiently varying color to cause the eye to wander. This effect is aggravated by the fact that the instrument is not a telescope, possessing no eye-piece or objective, so that the eye has to accommodate itself back and forth between the filament and the object studied.

The four-volt battery for the Holborn-Kurlbaum

lamps is here replaced by a battery of forty or fifty volts to run the spiral lamp, requiring a costly installation.

The Morse instrument was designed for use in hardening steel, and, throughout the limited temperature range required in this process, in spite of the crudities of construction above noted, this pyrometer may be read to about 3° C. within this range. Above 1100° C., however, it is very difficult and soon becomes impossible to make a satisfactory setting.

Tests of these spiral-filament lamps show that when aged at 1200° C. they will remain constant for several hundreds of hours within the range over which they are intended to be used.

It is interesting in this connection to note the behavior of ordinary incandescent lamps as to permanence.

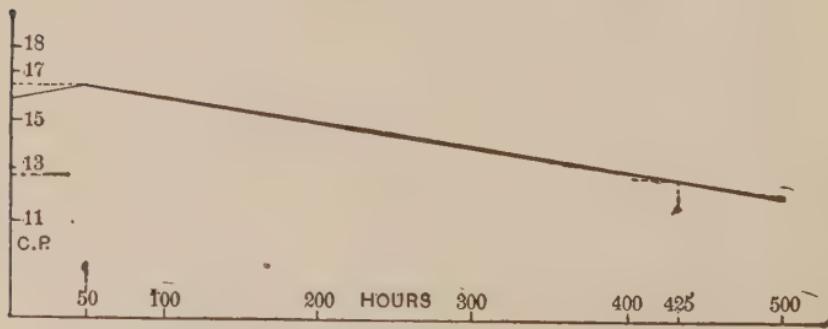


FIG. 54.

Conditions of Use.—The optical pyrometer, by reason of the uncertainty of emissive powers and of the relatively slight sensibility of the eye for comparisons of luminous intensities, cannot give as accurate results as the electric methods, although the accuracy attainable, since the satisfactory establishment of the laws of radiation throughout practically the attainable temperature range, is sufficient, as we have seen, when proper precautions are taken, for all industrial and most scientific needs.

The optical or radiation-pyrometer is peculiarly well adapted for many cases in which other methods fail, as when contact with the object whose temperature is sought cannot be made or when for any reason the pyrometer must be placed at a distance; for example, in the case of a moving body, as a rail passing into the rolling-mill; in the case of very high temperatures superior to the fusing-point of platinum, as of the crucible of the blast-furnace or that of the electric furnace; in the case of isolated bodies radiating freely into the air, as flames or wires heated by an electric current which cannot be touched without changing their temperature.

It is also convenient in the case of strongly heated furnaces, as steel and porcelain furnaces. But in this usage care must be taken to guard against the brightness of the flames, always hotter than the furnace, and against the entry of cold air. The arrangement with the closed tube described in connection with the heat-radiation pyrometer is indispensable if it is desired to obtain anywhere near exact results. Compared to this last pyrometer, the optical pyrometer has the advantage to require no installation in a fixed position. It has, on the other hand, the inconvenience to require a more active intervention on the part of the operator and can hardly be intrusted to a workman, while the set-up of the heat-radiation pyrometer may be made so that an observation reduces to a reading upon a scale.

Temperature of Flames.—Any substance inserted in a flame will take up a lower temperature than that of the flame itself, due to conduction, radiation, and diminished speed of the gas-stream around the body. Nichols, by using thermocouples of progressively finer wires, sought to determine true flame temperatures by extrapolating for a wire of zero diameter. The uncertainty of this method is

considerable although it gives consistent results, which are probably low.

The radiation methods have been employed by Lummer and Pringsheim, Kurlbaum, G. W. Stewart, and Féry. The temperature as given by an optical pyrometer will depend on the thickness and density of the flame as well as upon its reflecting and absorbing powers. The reflecting power of a flame is small and probably varies with the kind of flame; the results as yet obtained are quite discordant on this point.

Kurlbaum interposed a flame between a black body and the eye and assumed that the two were of the same temperature when the flame disappeared against its background. This method gave results lower than those obtained by Lummer and Pringsheim (p. 184). Kurlbaum and Stewart both claim that the carbon in the flame departs more widely from a black body than platinum, and the latter gets 2282 for the value of A in Wien's displacement equation $\lambda_m T = A$, assuming Nichols's value 1900° C. for the acetylene temperature. Féry has shown, however, that the brightness of the sodium line, measured with a spectrophotometer, is not increased by passing obliquely a beam from an electric light across the flame studied, seeming to indicate that the diffusing power is nil for the light coming from carbon. This would imply a value of A of the order of 2800, or of 2400° C. for the acetylene flame, assuming $\lambda_m = 1.05$.

Féry's method of measuring flame temperatures is to produce the reversal of a metallic line by means of light emitted by a solid body brought to the proper temperature. The image of the filament of an incandescent lamp is thrown by a large aperture lens onto the narrow slit of a spectroscope. The rays from the filament pass through the flame to be studied, which contains sodium or other

metallic vapor. When the filament is raised in temperature the *D* line, say, is ultimately reversed, and at the moment of disappearance the filament and flame are assumed to have the same temperature, which may be measured by sighting an optical pyrometer on the filament.

Some of Féry's results are as follows:

Bunsen	{	Open.....	1870° C.
		Half-open.....	1810
		Shut.....	1710
Acetylene.....			2550
Oxyhydrogen with illuminating-gas and oxygen.....			2200
Oxyhydrogen with $H_2 + O$			2420

For this determination, Féry used his absorption-pyrometer. The results obtained may be slightly high, but hardly by more than 100° C., as platinum may be melted in an open Bunsen.

All of the above methods assume that flames are non-luminescent, otherwise the results obtained are too high. Absurd results will also be obtained if the flames are colorless, i.e., contain no finely divided particles heated by the flame, as in an open Bunsen.

Measurement of the Relative Intensity of Different Radiations.—It is on this principle that rests the eye-estimation of temperatures, such as are made by workmen in industrial works. Numerous attempts, none very successful, have been made to modify this method and make it precise. There is need to consider this only from the point of view of a summary control over the heating of industrial furnaces.

a. Use of the Eye.—Pouillet made a comparison of the colors of incandescent bodies in terms of the air-thermometer. The table that he drew up is reproduced everywhere to-day:

First visible red.....	525°	Dull orange	1100°
Dull red.....	700	Bright orange	1200
Turning to cherry.....	800	White	1300
Cherry proper.....	900	Brilliant white	1400
Bright cherry.....	1000	Dazzling white	1500

The estimation of these hues is very arbitrary and varies from one person to another; more than that, it varies for the same person with the exterior lighting. The hues are different by day from those by night; it is thus that the gas-flame, yellow during the day, appears white at night. It is only in the reds that any accuracy can be had by the eye-method. Workmen can sometimes guess to better than 25° C. up to 800° C. At 1200° errors of over 200° will be made.

b. Use of Cobalt Glass.—One may exaggerate the changes of hue in suppressing from the spectrum the central radiations, the yellow and green for example, so as only to keep the red and the blue. The relative variations of two hues are the greater the more separated they are in the spectrum; now, the red and the blue form the two extremities of the visible spectrum.

It has been proposed for this purpose to use cobalt glass, which cuts out the yellow and green, but lets pass the red and blue. It must be remembered that the ratio of the radiations transmitted varies with the thickness of the glass as well as with their absolute intensities.

Let I_a and I_b be the intensities of the radiations emitted, k_a and k_b the proportions transmitted by the glass through a thickness 1. Through a thickness e the proportion transmitted will be

$$\frac{I_a k_a^e}{I_b k_b},$$

which will vary with e in all cases that k_a is different from k_b .

It results from this that two cobalt glasses, differing in thickness or in amount of cobalt, will not give the same results. So that if the cobalt glass habitually used is broken, all the training of the eye goes for naught.

Besides, cobalt has the inconvenience of having an insufficient absorbing power for the red, which predominates at the more ordinary temperatures that we make use of. It would be possible, without doubt, by the addition of copper oxide, to augment the absorbing power for the red.

One would have better and more comparable results by employing solutions of metallic salts or of organic compounds suitably chosen. But few trials have been made in this matter.

Apparatus of Mesuré and Nouel.—It is known that by placing between two nicols a plate of quartz cut perpen-

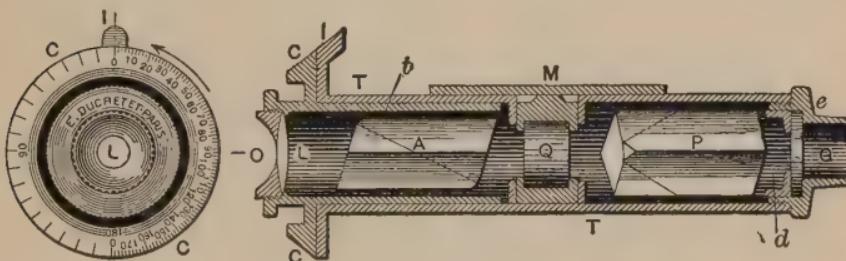


FIG. 55.

dicularly to the axis a certain number of the radiations of the spectrum are suppressed. This latter is then composed of dark bands whose spacing depends on the thickness of the quartz and the position of the angle of the nicols. Mesuré and Nouel have utilized this principle in order to cut out the central portions of the spectrum; this solution is excellent and preferable to the use of absorbing media. The apparatus (Fig. 55) consists essentially of a polarizer *P* and an analyzer *A*, whose adjustment to

extinction gives the zero of graduation of the divided circle CC . This circle is graduated in degrees and is movable before a fixed index I . Between the two nicols P and A is a quartz Q of suitable thickness, carefully calibrated. The mounting M allows of its quick removal if it is necessary to verify the adjustment of the nicols P and A . The quartz Q is cut perpendicularly to the axis. A lens L views the opposite opening C furnished with a parallel-faced plate glass or, where desired, with a diffusing-glass very slightly ground.

The relative proportions of various rays that an incandescent body emits varying with the temperature, it follows that for a given position of the analyzer A the composite tint obtained is different for different temperatures.

If the analyzer is turned while a given luminous body is viewed, it is noticed that the variations of coloration are much more rapid for a certain position of the analyzer. A very slight rotation changes suddenly the color from red to green. Now, if the analyzer is left fixed, a slight variation in the temperature of the incandescent body produces the same effect. The transmission hue red-green constitutes what is called the sensitive hue. There are then two absorptions, one in the yellow and the other in the violet.

This apparatus may be employed in two different ways. First fix permanently the analyzer in a position which gives the sensitive hue for the temperature that is to be watched, and observe the changes of hue which are produced when the temperature varies in one direction or the other from the chosen temperature. This is the ordinary method of use of this instrument. It is desired in a given manufacturing process (steel, glass) to make sure that the temperature of the furnace rests always the same; the instrument is adjusted once for all for this temperature. It

suffices to have but a short experience to train the eye to appreciate the direction of the change of hue.

The inventors have sought to make of their apparatus a measuring instrument; this idea is quite open to debate. In theory this is easy; it suffices, instead of having the analyzer fixed, to make it turn just to the securing of the sensitive hue and to note the angle which gives the position of the analyzer. But in fact the sensitive hue is not rigorously determinate and varies with the observer. A graduation made by one observer will not hold for another. It is not even certain that the same observer will choose always the same sensitive hue. At each temperature the sensitive hue is slightly different, and it is impossible to remember throughout the scale of temperatures the hues that were chosen on the day of the graduation. There is even considerable difficulty to recall this for a single temperature.

The following figures will give an idea of the differences which may exist between two observers as to the position of the sensitive hue:

Temperature.	Angle of Analyzer.	
	(1)	(2)
Sun.....	6000°	84 86
Gas-flame.....	1680	65 70
Red-hot platinum.....	800	40 45

The errors in the estimation of temperatures which result from the uncertainty of the sensitive hue will thus exceed 100°. With observers having had more experience the difference will be somewhat reduced, but it will remain always quite large.

Crova's Pyrometer.—Crova endeavored to give to the method of estimation of temperatures based on the unequal variation of different radiations of the spectrum a

scientific precision by measuring the absolute intensity of each of the two radiations utilized; but this method, from the practical point of view, does not seem to have given more exact results than the preceding ones.

The eye is much less sensitive to difference of intensity than to difference of hue, so that there is no advantage in making use of observations of intensity.

Crova compared two radiations,

$$\begin{aligned}\lambda &= 676 \text{ (red),} \\ \lambda &= 523 \text{ (green),}\end{aligned}$$

coming from the object studied and from the oil-lamp used as standard. For this purpose, by means of a variable diaphragm, he brings to equality one of the two radiations emanating from each of the sources, and measures afterwards the ratio of the intensities of the two other radiations.

The apparatus is a spectrophotometer. Placed before half the height of the flame is a total reflecting prism, which reflects the light from a ground glass, lighted by the radiations from an oil-lamp, having first passed through two nicols and a diaphragm of variable aperture. On the other half of the slit is projected by means of a lens the image of the body to be studied.

Before using the apparatus it is necessary to adjust the extreme limits of the displacement of the spectrum so as to project successively on the slit, in the focus of the eyepiece, the two radiations selected ($\lambda=676$ and $\lambda=523$). For this purpose there is interposed between the two crossed nicols a 4-mm. quartz plate which re-establishes the illuminations; for extinction again, the analyzer must be turned $115^\circ 38'$ for $\lambda=523$, and $65^\circ 52'$ for $\lambda=676$. The instrument is then so adjusted that the dark band

produced by the quartz is situated in the middle of the ocular slit.

The apparatus thus adjusted, in order to make a measurement at low temperatures, inferior to those of carbon burning in the standard lamp, one brings to equality the red radiations with the diaphragm, then, without touching the diaphragm again, the green is brought to equality by turning the *nicol*.

The optical degree is given by the formula

$$N = 1000 \cos^2 \alpha,$$

denoting by α the angle between the two principal sections of the *nicols*.

For higher temperatures the operation is reversed; one brings first the green to equality by means of the diaphragm, then the red to equality by a rotation of the analyzer. The optical degree is then given by the formula

$$N = \frac{1000}{\cos^2 \alpha},$$

and the rotation varying from 0° to 90° , the optical degrees vary from 1000° to infinity.

This method, which is theoretically excellent, possesses certain practical disadvantages:

1. Lack of precision of the measurements. In admitting an error of 10 per cent in each one of the observations relative to the red and green radiations, the total possible error is 20 per cent; now, between 700° and 1500° the ratio of intensities varies from 1 to 5: this leads to a difference of $\frac{1}{25}$ in 800° , or 32° .

2. Complication and slowness of observations. It is difficult to focus exactly on the body or the point on the body that one wishes to study. The set-up and the taking of observations sometimes require about half an hour.

3. Absence of comparison in terms of the gas-scale.

The *à priori* reason that had led to the study of this method was the supposition that, in general, the emissive power of substances was the same for all radiations and that consequently its influence would disappear by taking the ratio of the intensities of the two radiations. The measurements of emissive power given previously prove that this hypothesis is the more often inexact.

Action of Light on Selenium.—It has been known for a long time that light incident upon selenium changes the electric resistance of the latter, and pyrometers based on this principle have been devised. Light from an incandescent source whose temperature is sought falls upon a selenium cell forming part of an electric circuit in which are a battery and ammeter. As the light varies in intensity due to changes in temperature, the resistance of the selenium varies and the indications of the ammeter may be empirically calibrated in terms of temperature. As selenium is quite insensible to the invisible heat-waves, the lower limit of this method is above incandescence. Selenium also requires some time to recover its original resistance after being acted upon by light, and this lag might prove troublesome. As a dial instrument is used, the method could readily be made recording.

CHAPTER X.

EXPANSION- AND CONTRACTION-PYROMETERS.

Wedgwood's pyrometer, the oldest among such instruments, presents to-day hardly more than an historic interest, for its use has been almost entirely abandoned. It utilizes the permanent contraction assumed by clayey matters under the influence of high temperature. This contraction is variable with the chemical nature of the paste, the size of the grains, the compactness of the wet paste, the time of heating, etc. In order to have comparable results, it would be necessary to prepare *simultaneously, under the same conditions*, a great quantity of cylinders, whose calibration would be made in terms of the air-thermometer. Wedgwood employed cylinders of fire-clay, baked until dehydrated, or to 600° ; this preliminary baking is indispensable, if one wishes to avoid their flying to pieces when suddenly submitted to the action of fire. These cylinders have a plane face on which they rest in the measuring apparatus, so as always to face the same way (see the frontispiece). The contraction is measured by means of a gauge formed by two inclined edges; two similar gauges of 6 inches in length, one an extension of the other, are placed side by side; at one end they have a maximum separation of 0.5 inch, and at the other a minimum separation of 0.3 inch. Longitudinally the divisions are of 0.05 inch; each division equals $\frac{1}{240}$ of $\frac{2}{16}$ of an inch,

or $\frac{1}{1200}$ inch, which corresponds to a relative contraction of $\frac{1}{1200} \div \frac{5}{10} = \frac{1}{600}$ in terms of the initial dimensions.

We then have the following relation between the Wedgwood degrees and the linear contraction per unit of length:

Wedgwood.....	0	30	60	90	120	150	180	210	240
Contraction.....	0	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40

Le Chatelier has made experiments to determine the degrees of the Wedgwood pyrometer in terms of the scale of the air-thermometer by making use of clayey substances of different kinds, and in the first place of the cylinders from an old Wedgwood pyrometer of the Ecole des Mines. The contraction which accompanies the dehydration is quite variable with the nature of the pastes. In these experiments the time of heating was half an hour.

Centigrade temperature.....	600°	800°	1000°	1200°	1400°	1550°
Wedgwood.....	0	4	15	36	90	132
Argile de Mussidan.....	0	2	14	36	78	120
Limoges porcelain.....	0	0	2	21	88	91
Faïence de Choisy-le-Roi....	0	2	5	12	48	75
Faïence de Nevers.....	0	0	0	32	Melted	Melted
Kaolin.....	0	4	12	15	55	118
Clay.....	25	75	4	9	19	123
Titanic acid... 75						160

This table shows how variable are the observations; it is impossible, consequently, to compare the old measurements of Wedgwood and of his successors, because the manufacture of the cylinders has varied with the course of time.

Wedgwood had given a graduation made by a process of extrapolation which he has not explained, a graduation according to which he attributed 10,000° centigrade to 130° of his pyrometer, which corresponds to about 1550°. One might still seek to re-establish the graduation by utilizing the determinations of the fusing-points of the

metals made by Wedgwood, but the results are too discordant to warrant any definite conclusion. According to Wedgwood, copper would be more fusible than silver, iron would not be far removed from silver; it is probable that these observations were made with very impure metals, or at any rate were made with metals much oxidized before their fusion. In any case the cylinders which he made use of in his first experiments assume a much greater contraction than those of the pyrometer of the School of Mines whose graduation was given above. One might with considerable reserve indicate the following graduation for measurements made with the first cylinders employed about 1780:

Wedgwood degrees.....	0	15	30	100	140
Centigrade degrees.....	600	800	1000	1200	1400

The preparation of the cylinders was a most care-taking operation. Moulded in soft paste they were necessarily somewhat irregular. After the first baking they had to be trimmed to bring them to a uniform size. To-day, in several pottery works where the method is still employed, a much greater regularity is obtained by using a very dry paste, 5 per cent of water for example, moulding it under great pressure, about 100 kg. per square centimeter, in moulds of turned steel. The precision of the measurements is increased by augmenting the diameter, to 50 mm. for example. It is necessary at the same time to reduce the thickness to about 5 mm., in order that the compression be uniform throughout the mass.

This apparatus cannot be recommended in any instance as a true pyrometer, serving indirectly to evaluate temperatures in terms of the air-thermometer scale. The graduation is laborious and can only be made by means of the intermediary of another pyrometer; the use of fixed points

is not adapted for this graduation because the curve of contraction of clay in function of the temperature is too irregular for two or three points to determine it; in no case do the indications of this instrument possess any considerable precision.

But as simple pyroscope, that is to say, as an apparatus to indicate merely the equality or inequality of two temperatures, the Wedgwood pyrometer is very convenient.

It has the advantage of costing almost nothing and it is easy to use and within the comprehension of any workman. It seems to be particularly recommendable for certain ceramic industries, in which the ordinary pastes found there may be used to make the contraction-cylinders. It is necessary for this that the normal baking of these pastes is stopped at a temperature comprised within the period of rapid contraction. This is the case with fine faience and with ordinary earthenware. That would not be the case, however, for stanniferous faience nor for porcelain, because the baking of the first is stopped before the beginning of the contraction, and that of the second after its finish.

Expansion of Solids.—Some of the earliest forms of indicating-pyrometers were based on the

relative expansion of two metals, or of a metal and graphite or fire-clay. Some of these instruments have had and still



FIG. 56.

enjoy a very wide use both in Europe and America, and some of them are suitable for certain industrial processes not requiring exact temperature determination or control, as air-blasts. A common form of dial instrument is shown in Fig. 56. A tube of iron encloses a rod of graphite, and their differential expansion with change in temperature is communicated by levers to a pointer turning over a dial graduated in degrees. The upper limit of these instruments is about 800° C. (1500° F.), but they deteriorate rapidly when used at the higher temperatures. Their indications change with time due to changes produced in the materials by continued heatings. Correcting the zero of such an instrument, which should be done frequently, does not completely correct the rest of the scale, as the expansion properties of the two materials change differently with heating. Varying depths of immersion will also change the readings.

The Joly Meldometer.—A modified form of this instrument was previously mentioned, p. 195. As in its usual form, it may be of great service to chemists, metallurgists, and others in determining the melting-points and identification of minute specimens of minerals, salts, metals, and alloys, a further description may be of interest.

A platinum strip (Fig. 57) 10 cm. long, 4 mm. wide, and 0.02 mm. thick, is held between two clamps *C*, *C*, and kept under a slight tension by the spring *s*. A storage-battery current controlled by a small step rheostat *R* is sent through the platinum strip whose length at any instant is given by the micrometer screw *M*, whose contact is made appreciable by the closing of the circuit of an electric bell. The platinum strip is calibrated preferably by means of salts of known melting-points, as KNO_3 (399° C.), KBr (723°), and K_2SO_4 (1071°). Metals may also be used, but they tend to deteriorate

the platinum. The upper limit of the instrument is about 1500°C ., the Pd point being obtainable. Permanent elongation sets in somewhat before this point

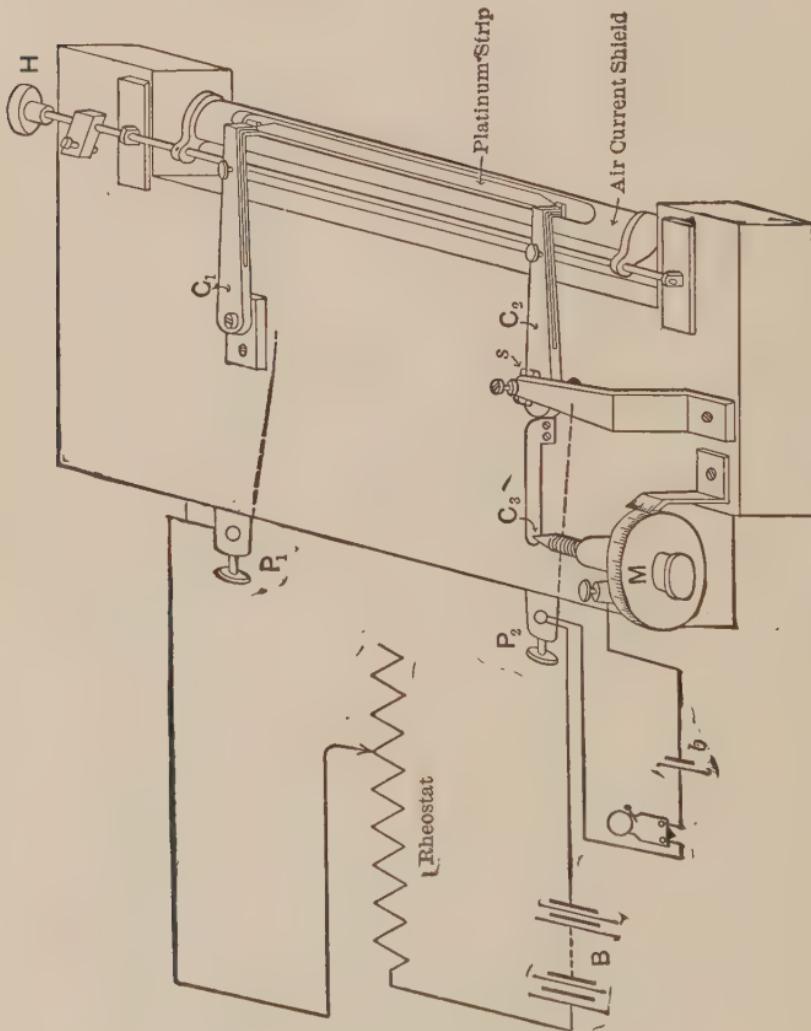


FIG. 57.—Meldomel.

is reached. The gold-point (1065°C .) can easily be determined to better than 2°C ., and only a few moments are required for an observation.

To take an observation, a speck of the specimen whose melting-point is sought is placed on the middle of the strip under a low-power microscope magnifying about twenty-five times. The current is increased and at the instant of melting, as observed with the microscope, the micrometer is set to make contact and read, when by interpolation, most conveniently made graphically, the temperature is found corresponding to the length of strip observed. This instrument gives a nearly but not quite linear relation between length of strip and temperature.

High-range Thermometers.—Although mercury boils normally at about 356° C., yet this liquid subjected to high pressure may be kept from boiling and, suitably enclosed, may be used as thermometric substance to much higher temperatures. Compressed under an atmosphere of some inert gas, as nitrogen or carbonic acid, and enclosed in a very hard glass, as Jéna 59^{III}, a borosilicate glass, the mercury-thermometer can be used up to 550° C. (1000° F.). The bulbs of such thermometers should be carefully annealed, before filling, at a temperature higher than the instrument is to be used, and the thermometer should also be annealed after it is made and allowed to cool slowly, otherwise considerable and irregular changes in its indications will occur, amounting to several degrees. The zero reading of such a thermometer should be taken after every observation in work of precision. If a considerable length of stem emerges into the air when taking a reading, a very considerable error, 25° C. or so, may be introduced at high temperatures due to the difference in temperature of the bulb and stem. This "stem correction" is very nearly:

$$\begin{aligned}\text{Stem correction} &= 0.00016 \cdot n \cdot (T - t)^\circ \text{ C.}, \\ &= 0.00088 \cdot n \cdot (T - t)^\circ \text{ F.},\end{aligned}$$

where n = number of degrees emergent from bath;

T = temperature of bath;

t = mean temperature of the emergent mercury column determined by some auxiliary means, as the faden-thermometer of Mahlke.*

The glass of mercury-thermometers has been successfully replaced by quartz, which is almost an ideal thermometric envelope, possessing an insignificant expansion and no appreciable zero lag, and capable of being used at very high temperatures. Such mercury-in-quartz thermometers are now constructed by Siebert and Kühn, and are graduated to about 700° C.

Dufour has tried to substitute tin for mercury-in-quartz thermometers, thereby attaining a temperature of over 1000° C. Such thermometers have not yet, however, come into use. It is a difficult matter not yet satisfactorily solved to find a substance suitable to use as thermometric fluid in quartz at high temperatures.

* Mahlke, *Zeitsch. f. Instru'k.*, p. 58, 1893.

CHAPTER XI.

FUSING-POINT, DILUTION-, AND TRANSPiration-PYROMETERS.

Fusing-point Pyrometry.—A long time ago it was proposed to compare temperatures by means of the fusing-points of certain metals and alloys. But the non-oxidizable metals are not numerous and all are relatively very costly: silver, gold, palladium, platinum. Use has, however, been made sometimes of these metals and their alloys, in admitting that the fusing-point of a mixture of two substances is the arithmetical mean of the points of fusion of the components, which is not quite exact. The use of these alloys is entirely abandoned to-day, and with reason.

By making use of metallic salts, among which a great number may be heated without alteration, one might constitute a scale of fusing-points whose employ would be often very convenient; but this work is not yet done, at least not in a sufficiently precise manner. To the separate salts may be added their definite combinations and their eutectic mixtures which have perfectly definite fusing-points. But one cannot take any mixture whatever of two salts, because in general the solidification takes place throughout a large interval of temperature and in a progressive manner.

Instead of utilizing the fusion of crystallized substances which pass abruptly from the solid to the liquid state, use may be made of the progressive softening of vitreous matters, that is to say, of mixtures containing an excess of one of the three acids, silicic, boric, or phosphoric. It is necessary in this case to have a definite process for defining a type degree of softening; a definite depression of a prism of given size is taken. These small prisms, formed of vitreous matters, are known under the name of *fusible cones*.

This method was first devised by Lauth and Vogt, who applied it in the manufactures at Sèvres before 1882. But they did not develop it as far as was possible; they were content to construct a small number of fusible cones corresponding to the various temperatures employed in the manufacture of the Sèvres porcelain.

Seger's Fusible Cones.—Seger, director of a research laboratory at the royal pottery works of Berlin, published, in 1886, an important memoir on this question. He determined a whole series of fusible cones of intervals of about 25°, including the interval of temperature from 600° to 1800°. The substances which enter into the composition of these cones are essentially:

Pure quartz sand;
Norwegian feldspar;
Pure carbonate of lime;
Zettlitz kaolin.

The composition of this last is:

SiO ₂	46.9
Al ₂ O ₃	38.6
FeO ₃	0.8
Alkalies.....	1.1
Water.....	12.7

In order to obtain very infusible cones, calcined alumina is added, and for very fusible cones oxide of iron, oxide of lead, carbonate of soda, and boric acid.

The shape of these cones (Fig. 58) is that of triangular pyramids of 15 mm. on a side and 50 mm. high. Under the action of heat, when softening begins, they at first contract without change of form, then they tip, bending over, letting their apex turn downwards, and finally flatten-

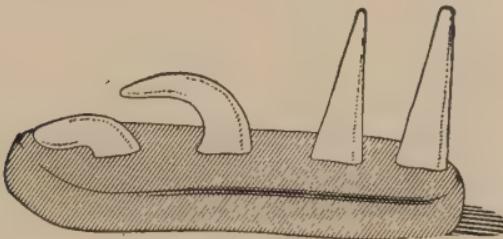


FIG. 58.

ing out completely. One says that the cone has fallen, or that it has melted, when it is bent half-way over, the point directed downwards.

The fusing-points of these substances have been determined at the Berlin porcelain works by comparison with the Le Chatelier thermoelectric pyrometer, previously described.

The cones are numbered, for the less fusible, which were first adjusted, from 1 to 38; this latter, the least fusible, corresponds to 1980° . The second series, more fusible, and established later, is numbered from 01 to 022; this last cone, the most fusible, corresponds to 590° .

If, instead of using the cones of German make, one wishes to make them himself in employing the same formulæ, it is prudent to make a new graduation. The

kaolins and feldspars from different sources never have exactly the same compositions, and very slight variations in their amounts of contained alkali may cause marked changes in the fusibility, at least for the less fusible cones.

It is to be noticed that in a great number of cones silica and alumina are found in the proportions $\text{Al}_2\text{O}_3 + 10\text{SiO}_2$. This is for the reason that this mixture is more fusible than can be had with silica and alumina alone. It is the starting-point to obtain the other cones, the less fusible by the addition of alumina, and the more fusible by the addition of alkaline bases.

The table on pages 266 and 267 gives the list of cones of Seger's scale.

These cones may be classed in a series of groups in each of which the compositions of different cones are derived from that of one of them, generally the most fusible, by addition in varying proportions or sometimes by substitution of another substance.

The cones 28 to 38 are derived from the cone 27 by the addition of increasing quantities of Al_2O_3 .

The cones 5 to 28 from the cone 5 by addition of increasing quantities of the mixture $\text{Al}_2\text{O}_3 + 10\text{SiO}_2$.

The cones 1 to 5 from the cone 1 by substitution of increasing quantities of alumina for the sesquioxide of iron.

The cones 010 to 1 from the cone 1 by the substitution of boric acid for silica.

The cones 022 to 011 from the cone 022 by the addition of increasing quantities of the mixture $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$.

Fig. 59 gives the graphical representation of these data; the ordinates are temperatures, and the abscissæ are values of x from the table.

These fusible cones of Seger are pretty generally used in the ceramic industry; they are very convenient in all

intermittent furnaces whose temperature has to increase constantly up to a certain maximum, at which point the cooling-off is allowed to commence. It is sufficient, before firing up, to place a certain number of fusible cones opposite a draft-hole closed by a glass, through which they may

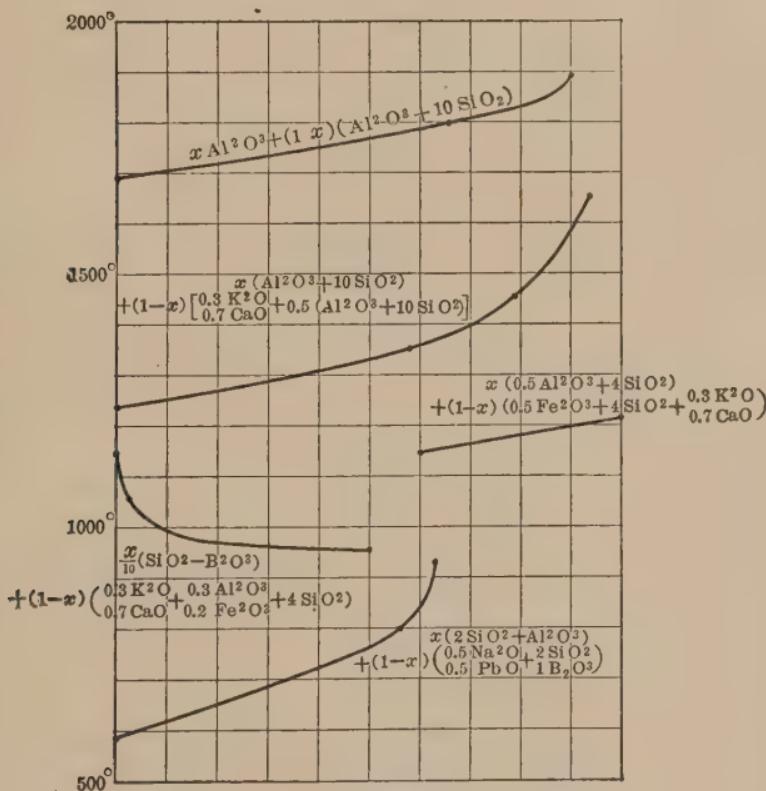


FIG. 59.

be watched. In seeing them fall successively, one knows at what moments the furnace takes on a series of definite temperatures.

In continuous furnaces, the cones may be put into the furnace during the process, but that is more delicate. It

is necessary to place them on little earthenware supports that are moved into the desired part of the furnace by an iron rod. When, on the contrary, they are put in place at the start in the cold furnace, they are held in place by a small lump of clay.

Nos.	Deg. T.	Composition.	X	Formulæ.
38	1890	1 $\text{Al}_2\text{O}_3 + 1 \text{ SiO}_2$	9	
36	1850	1 " + 1.5 "	8	
35	1830	1 " + 2 "		
34	1810	1 " + 2.5 "		
33	1790	1 " + 3 "		
32	1770	1 " + 4 "		
31	1750	1 " + 5 "		
30	1730	1 " + 6 "		
29	1710	1 " + 8 "		
28	1690	1 " + 10 "		
27	1670	1 { 0.3 K_2O } + 20($\text{Al}_2\text{O}_3 + 10 \text{ SiO}_2$) 0.7 CaO	0	
26	1650	1 " + 7.2 "	93	
25	1630	1 " + 6.6 "		
24	1610	1 " + 6 "		
23	1590	1 " + 5.4 "		
22	1570	1 " + 4.9 "		
21	1550	1 " + 4.4 "		
20	1530	1 " + 3.9 "		
19	1510	1 " + 3.5 "		
18	1490	1 " + 3.1 "		
17	1470	1 " + 2.7 "		
16	1450	1 " + 2.4 "		
15	1430	1 " + 2.1 "		
14	1410	1 " + 1.8 "		
13	1390	1 " + 1.6 "		
12	1370	1 " + 1.4 "		
11	1350	1 " + 1.2 "		
10	1330	1 " + 1 "		
9	1310	1 " + 0.9 "		
8	1290	1 " + 0.8 "		
7	1270	1 " + 0.7 "		
6	1250	1 " + 0.6 "		
5	1230	1 " + 0.5 "		
4	1210	1 " + 0.5 $\text{Al}_2\text{O}_3 + 4 \text{ SiO}_2$	0	
3	1190	1 " + { 0.45 $\text{Al}_2\text{O}_3 + 0.05 \text{ Fe}_2\text{O}_3 \} + 4 \text{ SiO}_2$	1	
2	1170	1 " + { 0.4 $\text{Al}_2\text{O}_3 + 0.1 \text{ Fe}_2\text{O}_3 \} + 4 \text{ SiO}_2$		
1	1150	1 " + { 0.3 $\text{Al}_2\text{O}_3 + 0.2 \text{ Fe}_2\text{O}_3 \} + 4 \text{ SiO}_2$		

$$X \text{Al}_2\text{O}_3 + (1-X)(\text{Al}_2\text{O}_3 + 10 \text{ SiO}_2)$$

$$X(\text{Al}_2\text{O}_3 + 10 \text{ SiO}_2) + (1-X)(0.3 \text{ K}_2\text{O} + 0.7 \text{ CaO} + 0.5(\text{Al}_2\text{O}_3 + 10 \text{ SiO}_2))$$

Nos.	Deg. T.	Composition.					X	Formulæ.
01	1130	1	$\{0.3 \text{ K}_2\text{O}\} + \{0.3 \text{ Al}_2\text{O}_3\} + \{0.2 \text{ Fe}_2\text{O}_3\}$	$\{3.95 \text{ SiO}_2\}$	$\{0.05 \text{ B}_2\text{O}_3\}$		1.05	
02	1110	1	"	"	"	$\{3.90 \text{ SiO}_2\}$		$\{0.10 \text{ B}_2\text{O}_3\}$
03	1090	1	"	"	"	$\{3.85 \text{ SiO}_2\}$		$\{0.15 \text{ B}_2\text{O}_3\}$
04	1070	1	"	"	"	$\{3.80 \text{ SiO}_2\}$		$\frac{X}{10}(\text{SiO}_2 - \text{B}_2\text{O}_3)$
05	1050	1	"	+1	"	$\{3.75 \text{ SiO}_2\}$	1.25	$+(1-X)\left(\begin{array}{l} 0.3 \text{ K}_2\text{O} \\ 0.7 \text{ CaO} \end{array}\right)$
06	1030	1	"	+1	"	$\{3.70 \text{ SiO}_2\}$		$+\left(\begin{array}{l} 0.3 \text{ Al}_2\text{O}_3 \\ 0.2 \text{ Fe}_2\text{O}_3 \end{array}\right) + 4\text{SiO}_2$
07	1010	1	"	+1	"	$\{3.65 \text{ SiO}_2\}$		
08	990	1	"	+1	"	$\{3.60 \text{ SiO}_2\}$		$\{0.35 \text{ B}_2\text{O}_3\}$
09	970	1	"	+1	"	$\{3.55 \text{ SiO}_2\}$		$\{0.40 \text{ B}_2\text{O}_3\}$
010	950	1	"	+1	"	$\{3.5 \text{ SiO}_2\}$	5	$\{0.45 \text{ B}_2\text{O}_3\}$
011	920	1	$\{0.5 \text{ Na}_2\text{O}\}$	$+0.8 \text{ Al}_2\text{O}_3$	$+ \{1.0 \text{ B}_2\text{O}_3\}$	$\{3.6 \text{ SiO}_2\}$	0.61	$\{0.5 \text{ PbO}\}$
012	890	1	"	+0.75	"	$\{3.5 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
013	860	1	"	+0.70	"	$\{3.4 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
014	830	1	"	+0.65	"	$\{3.3 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
015	800	1	"	+0.60	"	$\{3.2 \text{ SiO}_2\}$	0.57	$\{1.0 \text{ B}_2\text{O}_3\}$
016	770	1	"	+0.55	"	$\{3.1 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
017	740	1	"	+0.50	"	$\{3.0 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
018	710	1	"	+0.40	"	$\{2.8 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
019	680	1	"	+0.30	"	$\{2.6 \text{ SiO}_2\}$		$\{0 \text{ B}_2\text{O}_3\}$
020	650	1	"	+0.20	"	$\{2.4 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
021	620	1	"	+0.10	"	$\{2.2 \text{ SiO}_2\}$		$\{1.0 \text{ B}_2\text{O}_3\}$
022	590	1	"			$\{2.0 \text{ SiO}_2\}$	0	$\{1.0 \text{ B}_2\text{O}_3\}$

Wiborgh's Thermophones. — Another cheap, discontinuous pyrometer has been put on the market by Wiborgh. His thermophones are refractory earth cylinders 2.5 cm.

long and 2 cm. in diameter, containing an explosive. A thermophone is quickly deposited in the region whose temperature is sought, and the time noted to the fifth of a second until the cylinder bursts. A table then gives the temperature. Very concordant results are obtained if the thermophones are kept dry, different cylinders of the same set agreeing to $\frac{1}{5}$ sec, or 20° C. at 1000° C.

Dilution-pyrometers.—If a current of liquid or gas is kept flowing through a heated space it is evidently possible to estimate the temperature of the latter by observing the inlet and outlet temperatures of the fluid. Carnelly and Burton constructed such a pyrometer using water flowing at constant head from a tank kept at constant temperature. The graduation of such a pyrometer is purely empirical and may be effected, for a given heat and temperature of supply, by taking the inlet and outlet temperatures for three or more known temperatures of the furnace. For every different head and temperature of source the graduation will be different. Such a pyrometer evidently requires a somewhat cumbersome, permanent installation, and has the further disadvantages of not being direct-reading and having its indications change with difficultly controllable factors.

For determining hot-blast temperatures air-dilution pyrometers have been used, air from the outside entering the blast, mixing with it, and the temperature of the outgoing mixture being taken with a mercury-thermometer, and then the temperature of the blast computed from an empirical calibration. But very uncertain results can be obtained in this way, as they will depend on the speed of the blast, the size of openings, and the temperature of the diluting air.

Such a pyrometer is illustrated in Fig. 60.

Transpiration-pyrometers. — Various attempts have

been made to construct pyrometers based on the variation of the viscosity of gases with temperature, and this subject has been thoroughly studied by Barus and by Callendar; but owing to the complexity of the viscosity-temperature relation for small tubes, no simple pyrometer

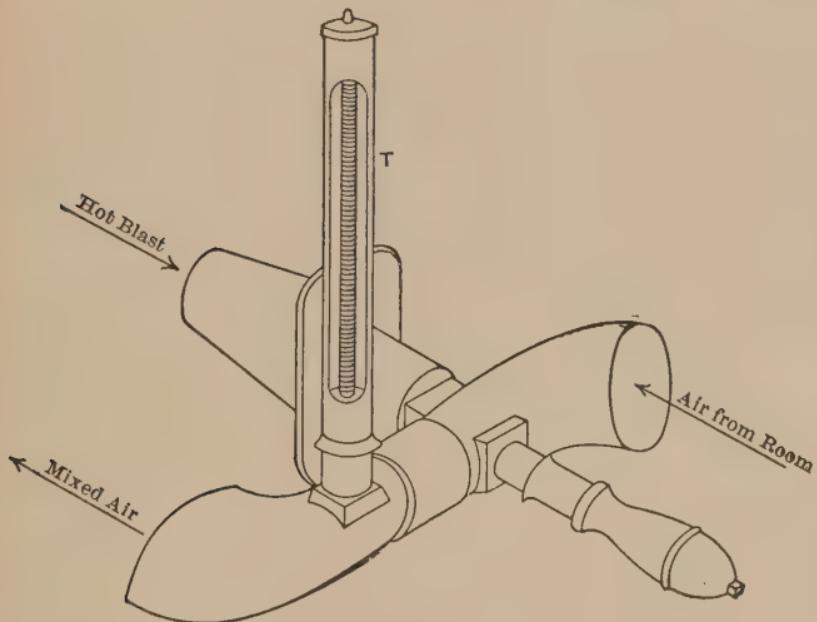


FIG. 60.

based on this relation alone, not requiring an arbitrary calibration, has been devised.

Job has shown that if a short piece of platinum wire be inserted in the end of a porcelain tube of less than 1 mm. diameter and a *constant* current of gas, as from an electrolytic cell or blower, be passed through this capillary, the back pressure developed will be proportional to the temperature, or $T = k(H - h_0)$, where H is given by a manometer inserted between the cell or blower and the porcelain capillary, and h_0 is the initial pressure. This simple relation holds very exactly up to temperatures as

high as 1500° C., and the method may be made very sensitive by a proper choice of manometer liquid and initial pressure h_0 . The indications, however, vary with the depth of immersion of the capillary, and they depend not alone upon the viscosity of the gas, but also upon the relative expansion of platinum and porcelain.

A pyrometer depending upon the change in pressure produced in a current of gas or vapor passing through a small orifice at high temperature has been developed by Uhling and Steinbart, using a steam-jet aspirator to produce a steady flow. Although simple in principle the apparatus as constructed is very complicated and costly. It is made direct-reading and also recording. The calibration is empirical and the apparatus is so constructed that temperatures are read off a water-manometer column. The elaborateness of construction of such a pressure apparatus renders it liable to deteriorate with time and use.

CHAPTER XII.

RECORDING-PYROMETERS.

AMONG the different methods for the measurement of high temperatures, some of them may be made continuously recording. This recording is as useful for industrial applications as for scientific investigations. In research laboratories one endeavors as much as possible to take observations automatically, escaping the influence either of preconceived ideas or of carelessness of the observer; in industrial works the use of such processes gives continuous control over the work of the artisans, such as the presence of no foreman can replace.

The record may be made by means of a pen or by photography. The former of these methods, more simple to handle, is preferable in works; the second, whose indications are more precise, is preferable in the laboratory. In general, however, one has not the choice, each phenomenon utilized in the measurements being treatable by only one method of registering. So far, only three among the different pyrometers have been rendered recording:

The gas-thermometer at constant volume;

The thermoelectric pyrometer;

The electrical-resistance pyrometer.

But, practically, the thermoelectric pyrometer has been most frequently used to take continuous records.

Recording Gas-pyrometer.—The transformation of the gas-thermometer into a recording instrument is extremely

simple and has been long since effected. It suffices to join permanently the tube from the porcelain bulb to a registering-manometer to realize a recording-pyrometer theoretically perfect. But practically these instruments possess many disadvantages that have prevented their introduction generally.

Above 1000° the permeability of the porcelain for water-vapor is sufficient to soon render them useless. Investigations made by the Paris Gas Company have shown that in furnaces heated to 1100° the penetration of water-vapor is sufficiently rapid so that in a few days liquid water collects in the cold parts of the apparatus.

Absolute impermeability of the apparatus, which is quite indispensable, since its operation supposes the invariability of the gaseous mass, is very difficult to obtain. Frequently the glazing of the porcelain has holes in it. The numerous joints entering into the registering apparatus, and above all the metallic parts of the apparatus, may be the seats of very small leakages difficult to locate.

The connection of the metallic parts with the porcelain tube is generally made with wax, always with substances of organic origin which, in the vicinity of industrial apparatus, generally bulky and thick-walled, cannot be protected against radiation save by a water-jacket. This is a serious inconvenience.

In laboratory apparatus of small size the protection of the joint is easier, but then the large dimensions of the bulb, as has been indicated, are a serious disadvantage. One cannot, in a small furnace, find a large volume whose temperature is uniform.

But the most serious disadvantage of the recording gas-pyrometer, and the principal reason for its abandonment, is the difficulty of its graduation. Already with the mercury-manometer the waste space is a source

of complications. However, this may be measured and allowed for. With the registering-manometer the waste space is much greater, and besides variable with the deformation of the elastic tube. Thus the graduation can be made only empirically, employing baths of fixed fusing- or boiling-points, an operation almost always impossible of realization with an apparatus of very fragile porcelain.

Electrical-resistance Recording-pyrometer.—After the gas-pyrometer, the oldest, we shall describe immediately the electrical-resistance pyrometer, which is the most recent.

In order to render his pyrometer recording (Fig. 61), Callendar employs the following very simple device: Two of the branches of a Wheatstone bridge used to measure the resistance of the heated coil are made of a single wire, on which slides a rider to which is brought one of the galvanometer leads. To each position of the rider, when the galvanometer is at zero, corresponds a resistance, and consequently a definite temperature of the coil. The position of the rider may be easily registered by attaching to it a pen writing on a sheet of paper which moves perpendicularly to the length of the wire. In order to have the curve thus obtained correspond to that of temperatures, it suffices that the position of the rider be at each instant adjusted so as to keep the galvanometer at zero.

This result is obtained by means of a clock-movement controlled by a relay that the galvanometer works in one direction or the other, according to the direction of the deflection that it tends to take on from the zero-point. It is a movable-coil galvanometer whose needle carries an arm which, making contact, causes a current to pass.

Fig. 62 gives an example of a curve recorded by this apparatus, showing the effect on the temperature of an

annealing-oven by firing by an old hand and by a new one.

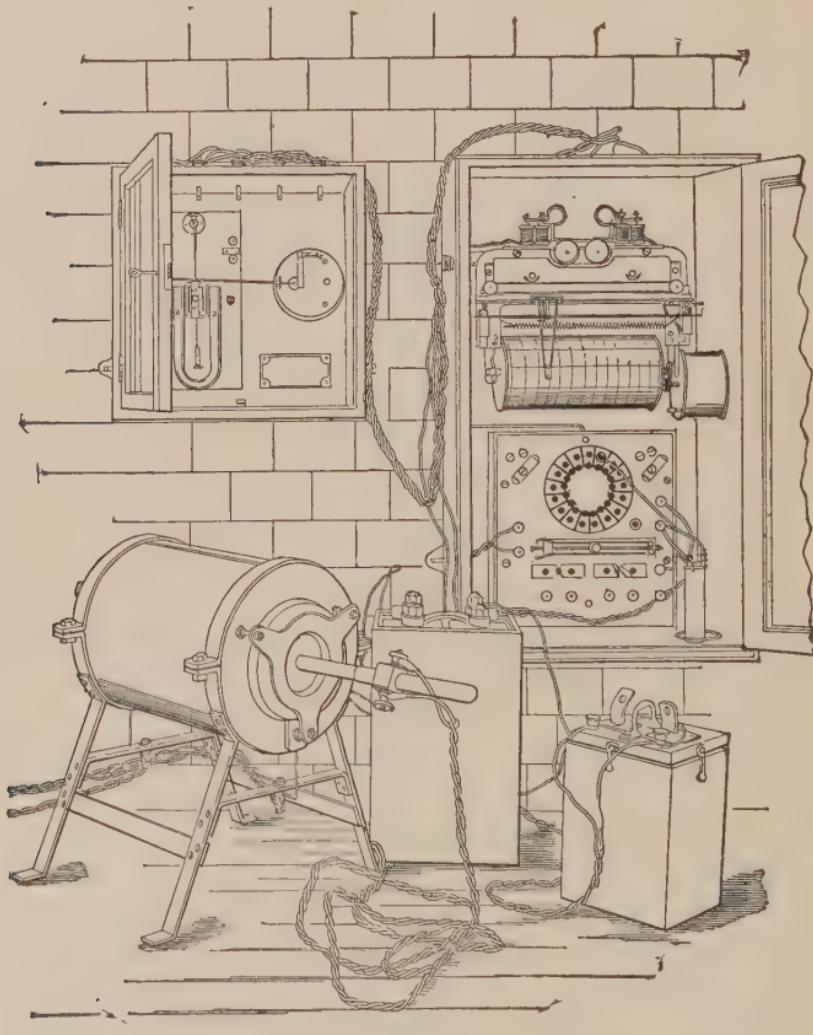


FIG. 61.

This registering apparatus is necessarily very costly, but it is actually the only sensitive one which effects the record of high temperatures by purely mechanical means, without the intervention of photography; it is possible that

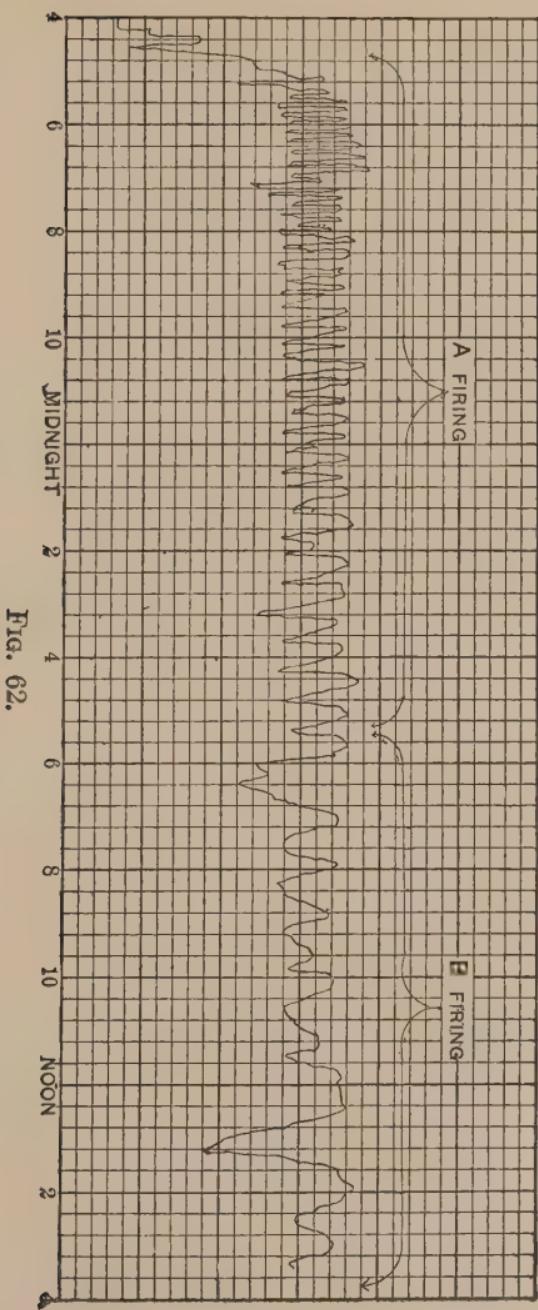


FIG. 62.

it will be used in certain large industrial works. For work in the laboratory it seems less convenient; the registering deprives the method of electrical resistances of the great precision which belongs to it and in which consists its great merit; there are also disadvantages, such as the necessity to use for the protection of the coil a fragile tube of porcelain of considerable volume.

This recorder possesses an interesting detail which assures good working and which could well be adopted in other similar cases. The pointer of the galvanometer-needle does not hit against a fixed conductor, to which it would stick on account of heating by the passage of the current and especially the extra current at break. This conductor consists of the metallic circumference of a wheel which is given a slow constant rotary motion, rendering all adherence impossible. This artifice renders possible working the relays by means of a sensitive galvanometer, which would not otherwise be realizable.

Callendar has applied the same method of recording to Langley's bolometer. The curve of Fig. 63 gives the record of solar radiation for a day.

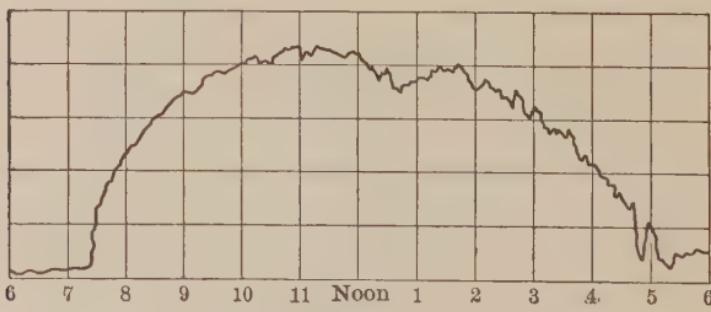


FIG. 63.

The same method of recording may be applied to the measurement of temperatures by means of thermoelectric

couples by using the method of opposition. But in this case the strength of the currents available to work the relays is much more feeble than in the preceding applications, so that a great sensibility cannot be obtained. Fig. 61 shows a Callendar recorder as made by the Cambridge Instrument Company, arranged for the thermoelectric measurement of temperatures in connection with an electric-resistance furnace.

Thermoelectric Recording-pyrometer.—The recording-pyrometers most currently in use to-day are the thermoelectric pyrometers recording photographically. Numerous attempts have been made to secure a recorder with a pen, as is done in the case of the recording-voltmeters and ammeters in use industrially, but, up to the present, with but limited success. The strengths of current which can be utilized are very weak; for a precision of 10° an apparatus sensible to $\frac{1}{40000}$ volt is necessary; the resistance of the galvanometer-coils should be considerable, 100 ohms at least, as has been previously explained, and the corresponding current will be only a millionth of an ampere. There are on the market such alleged recording-pyrometers, but they are for the most part constructed with galvanometer-coils of but few ohms' resistance and cannot give measurements of temperature exact to 100° . Siemens and Halske have recently, however, produced a recorder (Fig. 64), in which the pen touches the paper only momentarily, thereby increasing the possibilities of sensibility to that of a good millivoltmeter, *i.e.*, to 10° at 1000° C.

For the recording of temperatures one may seek two quite different results, to which are appropriate two methods of recording, equally different. One may desire to determine the temperature of a definite epoch, that is to say, to trace the temperature curve in function of the time.

This will be almost always the object in view in industrial works. It suffices, in this case, to let fall the luminous beam reflected by the galvanometer-mirror on a sensitive plate possessing a vertical movement of translation. The two coordinates of the curve thus recorded give, the one temperature, the other time. One may desire, on the other hand, to know the rate of variation of the temperature at a given instant, and at the same time the cor-

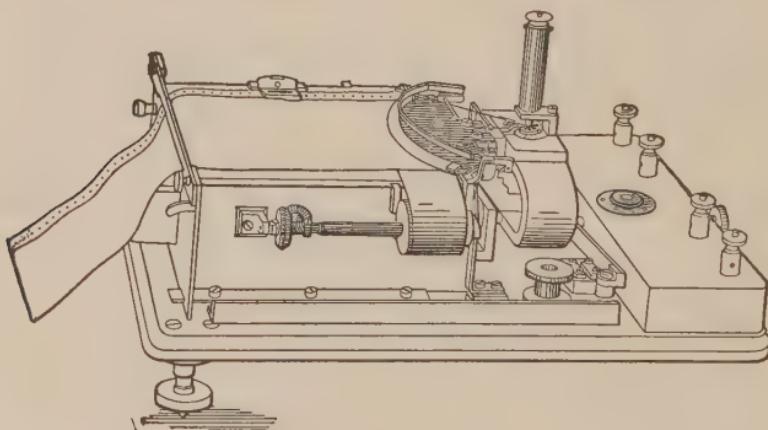


FIG. 64.

responding value of the temperature. This is the case in the greater number of laboratory investigations in which is desired the temperature at which a definite phenomenon occurs: fusion, allotropic transformation, etc.; and in order to recognize the occurrence of this phenomenon, use is ordinarily made of the accompanying absorption or liberation of latent heat, which is manifested by a variation in the law of heating or of cooling.

It is this latter method of recording that Le Chatelier first developed during his investigations on clays. A luminous beam reflected by the galvanometer-mirror falls periodically at regular intervals, of a second for in-

stance, upon a fixed sensitive plate. The distance apart of two successive images gives the variation of temperature during unit time, that is, the rate of heating or of cooling; the distance of the same image to the image corresponding to the beginning of the heating will give the measurement of the temperature.

In all cases of photographic recording it is necessary to replace the ordinary galvanometer-mirrors, which give images quite insufficient as to definition and brightness, by special mirrors made of a plano-convex lens, silvered on the plane surface. These mirrors are slightly heavier than parallel-face mirrors, but have two important advantages: the absence of extra images reflected by the front surface of the mirror, and a greater rigidity, which obviates accidental bendings of the mirror arising from the attachments to its support. One may easily get good mirrors of this type of 20 mm. diameter, and with more difficulty of 30 mm. diameter. These last give nine times more light than the mirrors ordinarily employed. It is easy to so choose the lens as to give a mirror of desired focal length. A plano-convex lens whose principal focus by transmission is 1 m. will give, after silvering the plane surface, an optical system equivalent to a spherical mirror whose radius of curvature would be 1 m.

Discontinuous Recording.—In this manner of recording, the *luminous source* should possess periodic variations; one of the simplest to employ is the electric spark between two metallic points. The interruption of the current is produced by a pendulum at definite intervals of time.

In order to have a spark sufficiently bright, it is necessary to use an induction-coil so worked as to give freely sparks of 50 mm., and to reinforce it by a Leyden jar which reduces the length of these sparks to 5 mm.; it suffices for this to use a jar of 1 to 2 liters. The choice of metals for

the points is equally important; zinc, aluminium, and especially magnesium give sparks that are very photogenic. These metals possess the disadvantage of oxidizing quite rapidly in the air, so that it is necessary from time to time to clean the points with a file. The metallic sticks may have 5 mm. diameter, and the distance apart of the points is 2 mm. One might without doubt, using mercury, which gives sparks as photogenic as does magnesium, construct an enclosed apparatus in which the metal would be preserved unchanged.

To produce the interruption there is attached to the

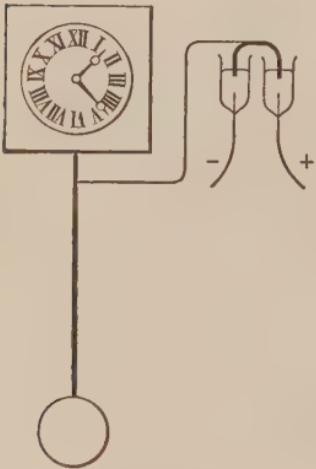


FIG. 65.

pendulum (Fig. 65) a vertical platinum fork which dips into two cups of mercury covered with alcohol. It is useful, in order to reduce to a minimum the resistance that the immersion of the fork opposes to the motion of the pendulum, to place this fork in the same horizontal plane as the axis of rotation of the pendulum. In this way one avoids the translatory movements in the mercury which cause the most trouble.

The only refinement with this intermittent lighting is to obtain, with a spark much too large and irregular to be photographed directly, the illumination of a very narrow slit. It is not sufficient to place the spark behind the slit and at a small distance away, because the slightest displacement of the spark would cause the luminous beam to fall outside of the mirror of the galvanometer. This difficulty is overcome by a well-known artifice. A lens is placed between the electrodes and the mirror (Fig. 66);

the position of the electrodes is so adjusted that the image of the mirror is formed between them. With a distance apart of the electrodes of 2 mm., a lens of 100 mm. focal length and a mirror of 25 mm. diameter, the image of the latter will touch the two points; the spark then necessarily crosses the image of the mirror, and the radiations passed by the lens will fall certainly upon the mirror. One is thus sure in placing before the lens a fine metallic slit

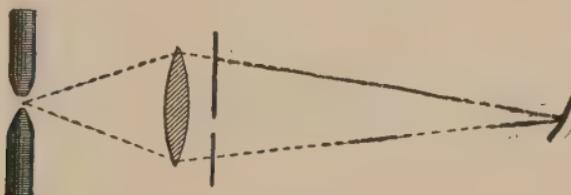


FIG. 66.

that all the rays transmitted will reach the mirror and will be sent to the photographic plate, and that whatever may be the position of the slit in front of the lens.

To save time it is advantageous to take several sets of observations on the same plate; this is easily done by arranging the plate so that it may be displaced vertically between two series, or in adjusting the slit so that it may be moved similarly before the lens.

The diagram (Fig. 67) is the reproduction of negatives relative to the action of heat on clays. The first line gives the graduation of the couple; it has been drawn from several different photographs which have been grouped to economize space. The following lines are reproductions of negatives made photographically without any intervention of the hand of the engraver. The second line, for example, represents the heating of an ordinary clay. A slight contraction of the lines between 150° and 350° indicates a first phenomenon with absorption of heat;

it is the vaporization of the enclosed water. A second cooling much more marked between 550° and 650° shows the dehydration, properly so called, of the clay, the liberation of the two molecules of water in combination. Finally, the considerable spacing of the lines at 1000° shows a sudden setting-free of heat corresponding to the isomeric change of state, after which the alumina becomes insoluble in acids. The other rows refer to the heating of

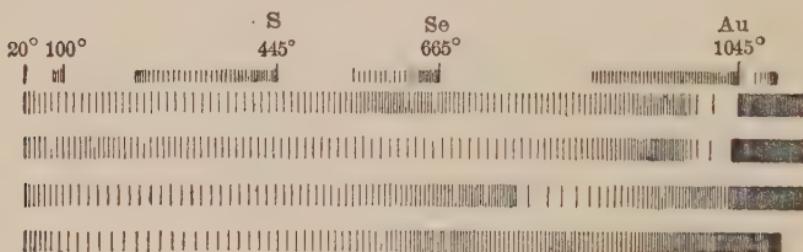


FIG. 67.

other varieties of clay, the third row to kaolin, the fifth to steargilite.

Continuous Recording.—The continuous recording of temperatures is of much more general usage, even in scientific laboratories, by reason doubtless of the greater simplicity of its installation. It has been studied especially by Roberts-Austen, late director of the royal mint at London. A vertical slit lighted from a convenient source projects its image, by means of the galvanometer-mirror, on a metallic plate pierced by a fine horizontal slit, and behind this slit moves a sensitive surface, plate or paper, which receives the luminous beam, defined by the intersection of the horizontal slit with the image of the vertical slit. If all were at rest, the impression produced by this luminous beam would be reduced to a point. If the plate alone is moved, a vertical straight line will be had; if the gal-

vanometer-mirror alone turns, a horizontal line. Finally, the simultaneous displacement of the plate and mirror gives a curve whose abscissæ represent temperatures, and whose ordinates, time. The illumination of the slit and the motion of the sensitive surface may be realized in many different ways.

Lighting of the Slit.—There are two quite distinct cases to consider, that of laboratory researches by rapid heating or cooling, which last only a few minutes, and that of continuous recording of temperatures in industrial works, which may last hours and days, that is to say, periods 100 times to 1000 times longer. The rate of displacement of the sensitive surface, and consequently the time of exposure to the luminous action, may vary in the same ratio. The luminous source necessary will be therefore quite different, depending upon the case. For very slow displacements it is sufficient to use a small kerosene-lamp with a flame of 5 to 10 mm. high. For more rapid displacements use may be made of an ordinary oil-lamp, an Auer burner, or an incandescent lamp; finally, for very rapid displacements of the sensitive plate, 10 mm. to 100 mm. per minute, one may advantageously employ the oxyhydrogen flame or the electric arc. For oxyhydrogen light the most convenient is the lamp of Dr. Roux, with magnesium spheres; it consumes little gas and is enclosed in a metallic box which prevents all troublesome diffusions of the light.

The electric arc gives much more light than is needed, and the rapid wearing away of the carbon, by displacing the positions of the luminous point, renders difficult the permanence of suitable illumination of the slit. For very short experiments one may very conveniently use the mercury-lamp in *vacuo* (Fig. 68) or the arc playing between two mercury surfaces. In order to run it, 3 amperes at 30 volts are requisite. Its only disadvantage is to go

out after running a few minutes on account of the evaporation of the mercury in the central tube. It suffices,

it is true, to give it a slight jar to make it go again, by causing a small quantity of mercury to pass from the outside annular space into the central tube. Special forms of mercury-lamp exist, however, which are free from this trouble.



FIG. 68.

Whatever the luminous source employed, the slit may be always lighted by means of a lens arranged as was indicated for discontinuous recording, that is, projecting upon the galvanometer-mirror the image of the luminous source. When this is large enough, it suffices to place the slit before the luminous source, bringing it up close enough so as to be sure that some of the luminous rays, passing through, fall upon the mirror. But there is danger here of so considerably heating the slit that it may be altered; for this reason one is led to use more voluminous light-sources than would otherwise be necessary. In the case of the use of a lens, the useful luminous intensity is as great as in placing the slit immediately next to the luminous source, so long as the image of the latter is greater than the galvanometer-mirror; now with the ordinary dimensions of the sources employed this condition is always fulfilled without any special precaution.

Instead of a slit lighted by a distinct luminous source, use may be made of a platinum wire, or better, as does Charpy, employ a carbon filament of an incandescent lamp heated by an electric current.

In order that the line traced by the recorder be very fine, it is necessary that the two slits, the luminous slit and the horizontal slit, be equally fine. Skilful mechanicians

can cut such slits in metals. But it is easier to make them by taking a photographic plate of bromide-gelatine that has been exposed to the light, developing until completely black, then wash and dry. By cutting the gelatine with the point of a penknife guided by a ruler, one may get transparent slits of a perfect fineness and sharpness.

Sensitive Surface.—For sensitive surfaces use is made of plates or films of bromide-gelatine. Professor Roberts-Austen employed exclusively plates which permit more easily the printing of a great number of positive proofs. Charpy, in his researches on the tempering of steel, made use of sensitive paper, which permits a much more simple installation.

Paper.—For industrial recording, paper would allow of the employing large rolls lasting several days, as in the recording magnetic apparatus of Mascart. But in general one wants to have quickly the results of the record; this is always the case in laboratory investigations, and almost always in industrial studies. It is thus preferable to be content with quite short bands of paper rolled on a cylinder. There exists such a model quite well known and easy to use: the recording-cylinders with an interior clock-movement of the firm Richard, Paris. They may be ordered from the maker with any desired rate of rotation; unfortunately this rate cannot be changed at the pleasure of the operator, a desideratum in laboratory investigations.

Fig. 69 represents the installation of the recording-pyrometer used by Charpy in his researches on the tempering of steel. To the right is the galvanometer, to the left the Richard recording-cylinder, and in the middle the electric furnace used for heating the samples of steel.

Plates.—The plate may be placed in a movable frame regulated by a clock-movement; this is the first arrangement.

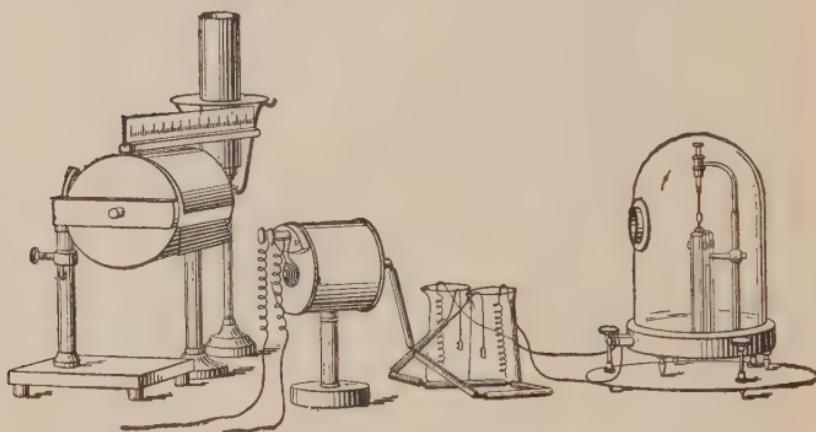


FIG. 69.

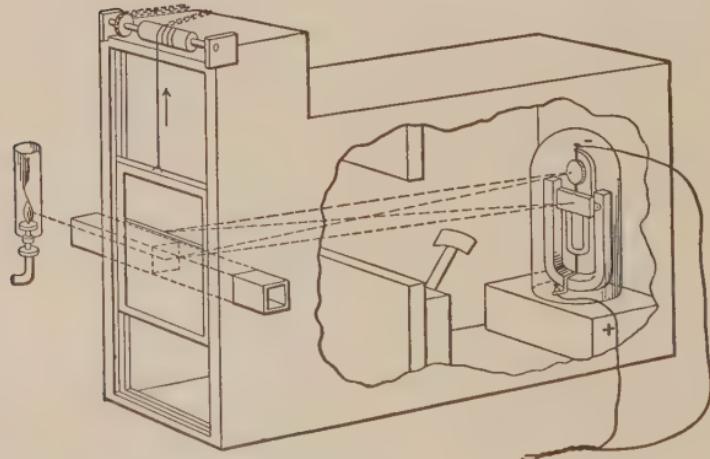


FIG. 70.

ment employed by Prof. Roberts-Austen (Fig. 70). But this installation, somewhat costly and complicated, has the same disadvantage as the recording-cylinders in that but

a single speed can be given to the sensitive surface. In order to drive the plate, Roberts-Austen later used a buoyed system in which the rate of rise of level of the water is controlled at will by the agency of a Mariotte's flask and a simple water-cock. The plate is kept in an invariable vertical plane by means of two lateral cleats whose friction is negligible on account of the mobility of the float. The sketch (Fig. 71) gives the arrangement of a similar apparatus made by Pellin for the laboratory of the Collège de France. It carries a 13×18 cm. plate which is attached to the float by means of two lateral springs not shown in the sketch. Neither are the two guides of the float, immersed in water, indicated; the play next the cleats is only two tenths of a millimeter. The uncertainty that this play can cause in the position of the plate is quite negligible. The curve (Fig. 72) is the reproduction of an experiment made with such an arrangement by Roberts-Austen on the solidification of gold.

During the whole period of freezing, the temperature remained stationary, then lowering of temperature was produced at a regularly decreasing rate as the temperature of the metal approached that of the surroundings.

It is indispensable to trace on each sensitive surface on which is to be recorded a curve, the line corresponding to the surrounding temperature, or at least a parallel reference line. This is very easy in the case of the guided plate or of the paper rolled on a cylinder. It suffices, after having brought the couple to the temperature of its

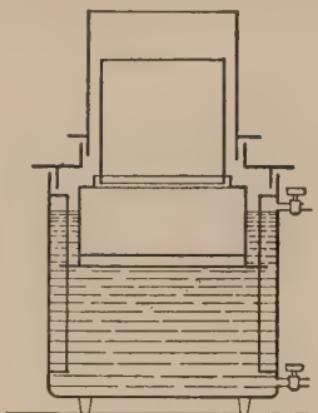


FIG. 71.

surroundings, to displace in the opposite direction the sensitive surface; the second curve traced during this inverse movement is precisely the line of the zero of the graduation of the temperatures. But this is a dependence that may be evaded by registering at the same time as the curve a reference line by means of a fixed mirror attached to the galvanometer in the path of the luminous beam which lights the movable mirror. Roberts-Austen like-

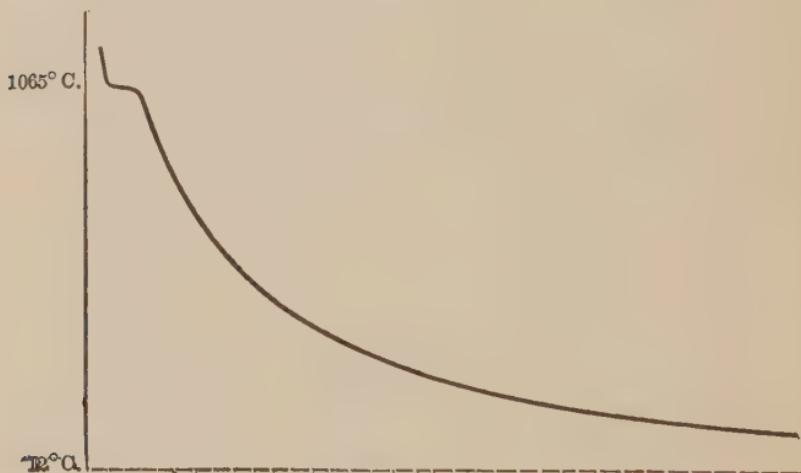


FIG. 72.

wise makes use of the luminous beam reflected by the fixed mirror to inscribe the time in a precise manner. A movable screen driven by a second pendulum cuts off at equal intervals of time this second luminous beam. The reference line, instead of being continuous, is made up of a series of discontinuous marks whose successively corresponding parts are at intervals of one second as is shown in Fig. 72.

The curves once obtained must be very carefully examined to recognize the points where the gradient presents slight anomalies, characteristic of the transforma-

tions of the body studied. Generally these irregularities are very insignificant, and it would be well, in order to recognize them with certainty, to obtain curves traced on a much greater scale. Practically this magnification is not possible without auxiliary devices which limit either the range or the sensibility; thus the sensitiveness of the galvanometer may be increased, and thus the deflection, but then for the greater range of temperature the luminous image would fall off the sensitive plate. Prof. Roberts-Austen has overcome this difficulty in an ingenious manner. He no longer registers the temperature of the body, but the difference between this temperature and that of a neighboring body which presents no transformation, platinum for instance. This difference of temperature, always small, may be recorded by a very sensitive galvanometer. If, at a given moment, the body, other than the platinum, undergoes a change of state accompanied by even very weak heat phenomena, the difference of the two temperatures, by reason of its small value, will undergo variations relatively very great. If it is desired not merely to recognize the existence of a phenom-

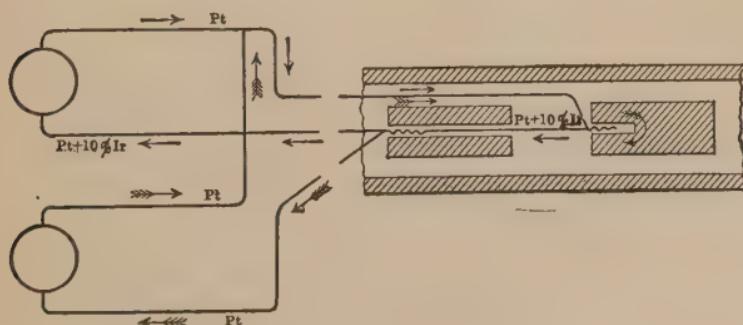


FIG. 73.

enon, but besides to measure the temperature at which it is produced, it is necessary to employ simultaneously

a couple connected to another galvanometer. With three leads, two of platinum and one of platinum-rhodium, a complex couple may be made, giving simultaneously the actual temperatures and the differences of temperature of two neighboring bodies. The diagram (Fig. 73) gives

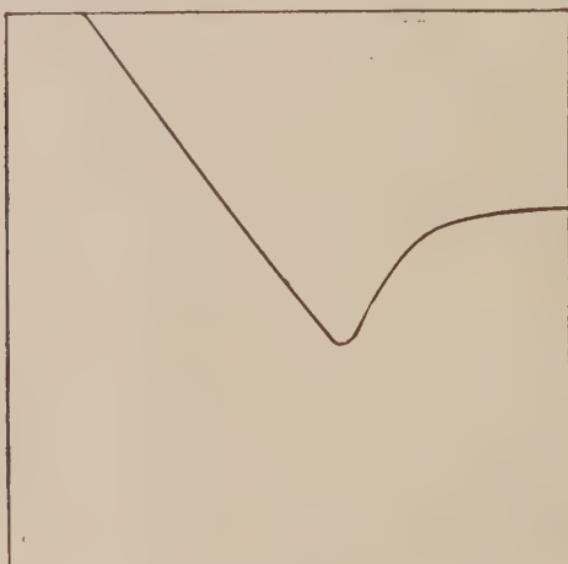


FIG. 74.

an idea of this arrangement which has proved very useful in the hands of Roberts-Austen for the study of alloys, and particularly for the study of the transformations of irons and steels. The curve of the solidification of tin is reproduced in Fig. 74, as obtained by this method. The double inflection indicates the existence of marked under-cooling; the tin, before freezing, is lowered to 2° below its fusing-point, to which it returns suddenly as soon as solidification sets in.

Recording pyrometers have been for the most part employed up to the present only in scientific laboratories. There exist, however, a few in metallurgical works, as the

blast-furnaces at Clarence Works of Sir Lothian Bell, the blast-furnaces of Dowlais and in the Creusot steel-works. The curves of Fig. 75 give an example of the curves obtained at Clarence Works; the lower curve gives the

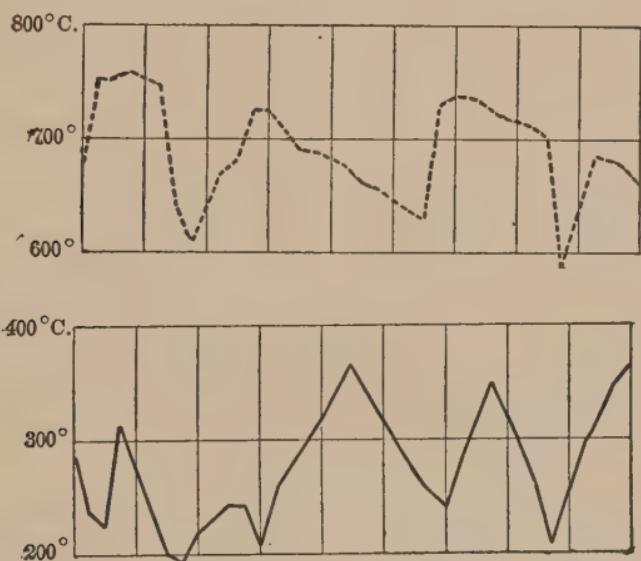


FIG. 75.

temperature of the gas at the furnace-mouth, and the upper curve that of the hot blast.

Modifications of Sir Roberts-Austen's Recorder.—The principal source of trouble with the autographic apparatus of Sir Roberts-Austen is the difficulty in giving a uniform steady motion to the photographic plate and also the necessity of additional graphical construction when phenomena involving differences of temperature are studied, as the critical points of steels.

Mr. Saladin of the Creusot Works and also Prof. Le Chatelier have devised a method which permits the photographic plate to remain fixed in position and in so placing the two galvanometers as to cause the lumi-

nous beam reflected by one mirror to be deflected horizontally, while the beam reflected by the other mirror is

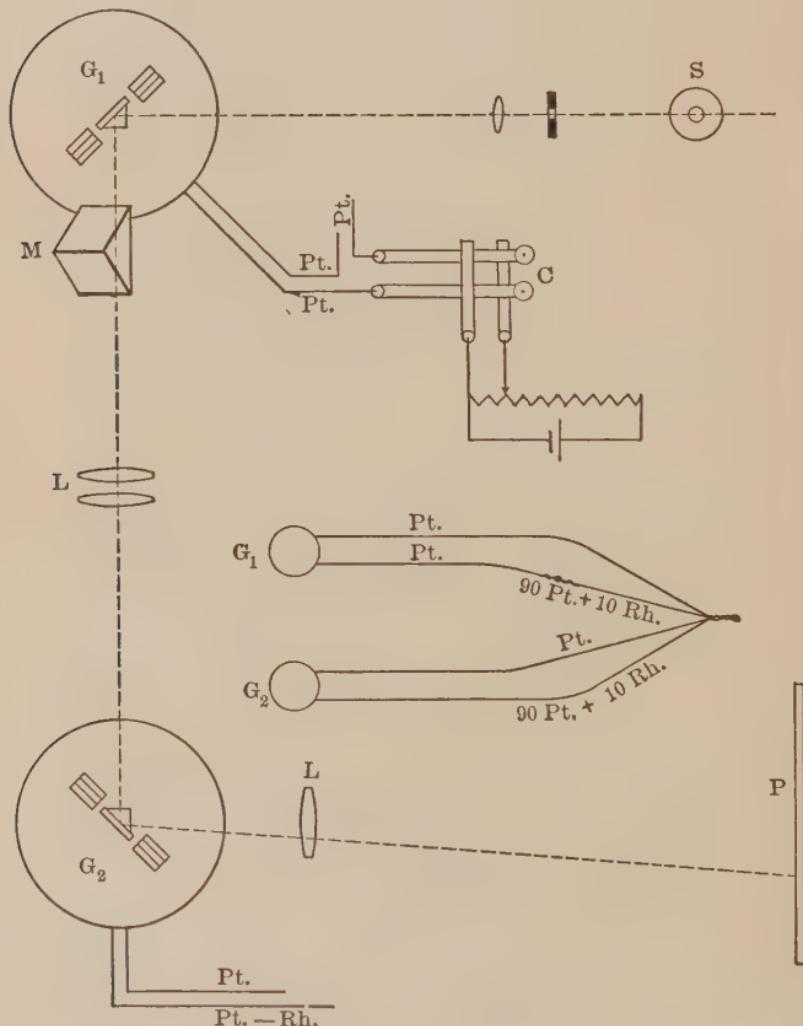


FIG. 76.

deflected vertically. It is an application of the principle of Lissajoux. The arrangement of the apparatus is as shown in Fig. 76.

Light from the source *S* (Fig. 76), an acetylene flame for instance, strikes the mirror—here a right-angled prism, to give better definition—of the sensitive galvanometer *G*₁, whose deflections measure the differences in temperature between the piece of steel or other object whose critical points are under observation and the comparison block, which may be platinum, quartz, or a 25 per cent nickel steel which has no critical point above 0° C.

The horizontal deflections of the beam of light are now turned into a vertical plane by passing through the totally reflecting prism placed as shown at *M*.

A second galvanometer, whose deflections are a measure of the temperature of the sample and whose mirror is at right angles to the first, reflects the incident beam horizontally which is focussed by the lens *L*, upon the ground-glass screen or photographic plate at *P*. The spot of light has thus impressed upon it two motions at right angles to each other, giving, therefore, a curve whose abscissæ are proportional to the temperature of the sample, or more strictly to the E.M.F.'s generated by the thermoelectric couple, and whose ordinates are proportional to the differences in temperature between the sample and the comparison block. At the beginning of each experiment, if a permanent record is desired, two axes are traced on the photographic plate by a slight deviation of the galvanometer-mirrors, and this can readily be produced by sending through them successively two currents of equal intensity, but of opposite direction, using a commutator *C* for this purpose.

In Saladin's apparatus the two galvanometers are each at a conjugate focus of a lens *L*, but in Le Chatelier's form the galvanometers are brought close together and the lens *L* omitted, forming a compact apparatus mounted

in a small portable case having a glass front which carries the two lenses required for the projection.

The sensitiveness of the method depends upon the sensitiveness of the galvanometer G_1 , which may be readily made to give five or six millimeters for each degree centigrade.

CHAPTER XIII.

STANDARDIZATION OF PYROMETERS.

Fixed Points.—As the scale determined by the gas-thermometer is the one universally recognized, it is necessary in order to graduate a pyrometer, to express its indications in terms of the gas-scale. In general it is not feasible to compare the readings of a pyrometer directly with those of the gas-thermometer. The use of the latter becomes restricted mainly to the establishment of certain constant reproducible temperatures or fixed points such as are given by freezing-points and boiling-points of the chemical elements and of certain compounds. The accuracy attainable in pyrometric researches is, therefore, limited by the exactness of our knowledge of these reference temperatures, and their determination has been and still is of the most fundamental importance in pyrometry. There have been a great many temperatures suggested for this use, but the actual number available is very small. Preference should be given to those determinations made with the gas-thermometer, although there are others made indirectly in terms of the gas-scale, as with thermo-couples and resistance-thermometers, which are of considerable weight.

We have already called attention to many of these determinations, among which the following are to be considered:

Sulphur.—(Boiling) 444°.6 C. under a pressure of 760 mm. with a variation of 0°.095 per millimeter change of mercury in the atmospheric pressure.

The boiling-point of sulphur has been the object of several series of distinct observations, among which we may cite:

Regnault.	448°
Crafts.	445
Callendar and Griffiths.	444 .5
Chappuis and Harker.	444 .7
Rothe.	444 .7

Regnault's figure was obtained by plunging the reservoir of the thermometer in the liquid sulphur; but this liquid will superheat, and so gives too high a value. The other three very concordant results were obtained in the vapor. The sulphur-point is easy to get experimentally if care is taken to guard against superheating and if a considerable volume is used commercial sulphur is sufficiently pure for this purpose. Electrical heating can be used to advantage, which is also true for the establishment of the other fixed points.

The result first published by Chappuis and Harker, using a constant-volume thermometer, was 445.2, but this difference from Callendar and Griffiths' result was shown probably to be mainly due to an incorrect value assumed for the expansion coefficient of the porcelain bulbs used by the former.

Callendar and Griffiths worked with a constant-pressure thermometer and it is of interest to note that the outstanding difference between the two most reliable experimental determinations by the constant-volume and constant-pressure methods is of the order of difference between the two gas-scales—constant volume and con-

stant pressure—as seen from Callendar's table (p. 32). In fact, in work of the highest precision it will probably soon be necessary to reduce observations to the thermodynamic scale.

Zinc.—(Freezing) 419°.0 C. Freezing-points undergo unappreciable changes with variations in atmospheric pressure and their experimental determination is somewhat easier than for boiling-points if a thermocouple is used. The direct determination of a metallic freezing- or melting-point with a gas-thermometer is beset with almost insurmountable experimental difficulties, so recourse is always had to some auxiliary pyrometer whose indications have been exactly calibrated by direct comparison with a gas-thermometer.

Zinc is easily gotten in sufficient purity. Some recent determinations of this point are:

Heycock and Neville.	419°.0 C.
Stansfield.	418 .2
Holborn and Day.	419 .0

The method employed by Stansfield, recording thermocouple, was not as reliable as those of the other two, the first of whom used a platinum resistance thermometer calibrated at the points 0°, 100°, and 444°.53, and the last, Holborn and Day, thermocouples compared directly with their constant-volume nitrogen-platinum-bulb thermometer.

Zinc.—(Boiling) 920° C. with a variation of 0°.15 for a change of 1 mm. in the atmospheric pressure.

The boiling-point of zinc has been the object of probably more determinations than any other, and yet it is the least best known and consequently the most unreliable to try and use, and is not to be recommended. It has been the object of so much study, undoubtedly, as

it was apparently the one point near the upper limit of the gas-thermometer which could be determined directly by this instrument, but superheating effects in vapors at such high temperatures and an even temperature distribution are very difficult to obtain even with electrical heating.

Some of the results obtained are shown by the following table:

E. Becquerel	930° and 890° C.
Sainte-Claire-Deville.	915 to 945
Barus.	926 and 931
Violle.	930
Holborn and Day.	910 to 930
Callendar.	916
D. Berthelot.	918

The value 930° as given by Violle's and Barus' results was generally accepted until recently, but the more recent determinations indicate 930 to be over 10° high. The value adopted, 920°, is probably not in error by over 5° C.

Gold.—(Fusion or Freezing) 1065° C. This point is today one of the best-known fixed points, and gold possesses the advantages of being obtainable in very great purity, is not oxidizable in air, nor is it readily attacked by the silicious materials used in crucibles, etc. Its cost is its only drawback for use in considerable quantities, but methods have been devised, as inserting a short length of wire between the leads of a thermocouple, requiring only very minute amounts of gold. These wire methods give the same results as the crucible method, as shown by Holborn and Day and by D. Berthelot.

The early determinations of the gold-point were quite discordant, but the later ones where electric heating was employed are in excellent agreement.

Pouillet.	1180° C.
E. Becquerel.	1092 and 1037
Violle.	1045
Holborn and Wien.	1070 to 1075
Heycock and Neville.	1062
D. Berthelot.	1064
Holborn and Day.	1064
Jacquierod and Perrot.	1067

Violle's value was long quoted as the best for the gold-point, but the later determinations show it to be 20° low. Holborn and Wien's high value was obtained with a porcelain-bulb thermometer and is to be considered as replaced by Holborn and Day's value, to obtain which nitrogen in a Pt-Ir bulb was used, together with a thermocouple. The agreement of their results when working under various conditions is shown from the following observations:

Gold, sample 1.	1064.0 \pm 0.6	(crucible method)
" 2.	1063.5	" "
" 2.	1063.9	(wire method)

Not less than 300 grammes was used for observations in both graphite and porcelain crucibles, while by the wire method 0.03 gramme of the metal suffices.

Berthelot used his optical gas-pyrometer in connection with thermocouples and considers his result to be in error by less than 2°. Heycock and Neville's result was obtained by extrapolation above the sulphur-point of the platinum resistance formula, while Jacquierod and Perrot's value was obtained in terms of a quartz-bulb constant-volume thermometer filled with various gases, the results agreeing to a few tenths of a degree. They used a modified form of the wire method, which consisted in making a small piece of gold wire a part of an alternating electric

circuit, melting of the gold being noted by cessation of sound in a telephone.

Berthelot has called attention to the fact that these later determinations are sufficiently concordant to warrant reducing them to the thermodynamic scale (see p. 33).

Observer.	Gas.	Initial Pressure.	Corrections.	Observed Temp.	Thermo-dynamic Temp.
D. Berthelot. . . .	Air	76 cm	+1°.36 C.	1064	1065.6
Holborn and Day	N	29 "	0 .27	1064	1064.3
Jacquierod a n d { Air, N, }	{ O, CO	23 "	0 .21	1067.2	1067.4
Perrot.					

Silver.—(Freezing) { 955 in air } { 961.5 pure }. The freezing-point of silver is not a constant temperature except under very definite conditions, and this metal is volatile, thus making it unsafe to use where its vapors may attack platinum wires, as of a thermocouple whose electric properties silver alters very considerably.

Many determinations of this point have been made, but it is only the recent observations that take into account the effects of oxidizing and reducing atmospheres.

	Pure Ag.	In Air.
Pouillet.	1000° C.
E. Becquerel.	960 and 916
Violle.	954
Holborn and Wien.	970	...
Heycock and Neville.	960.5	955
D. Berthelot.	962	957
Holborn and Day.	961.5	955

Melted silver exposed to the air gradually absorbs oxygen, which lowers the freezing-point, and this latter

is not a definite temperature varying with the rate of cooling, mass, and surroundings. The wire method gave 953.6 ± 0.9 as found by Holborn and Day. The freezing-point of *pure* silver may be obtained in a graphite crucible in an atmosphere of nitrogen, *i.e.*, in conditions preventing oxidation. The uncertainty of surely realizing a definite temperature with silver renders it less desirable than gold.

Copper.—(Freezing) 1065° in air, 1084° pure. Whether or not the gold- or the copper-point was the higher was long an open question in pyrometry. The only advantage in practice of copper is its cheapness, but the fact that copper has two freezing-points does not possess the same disadvantages as with silver, for the copper-points are very definite, the higher one, 1084 , being that of the pure metal, easiest obtained with a graphite crucible, the metal being protected from the air by a layer of powdered graphite. The lower value, 1065 , is given by the wire method and copper may replace gold in this way. Values intermediate between 1065 and 1084 will be obtained for incomplete protection from air, the effect being due, as explained by T. W. Richards, to the formation and solution of cuprous oxide, saturation of the copper with the oxide giving the point 1065 .

We may note the following determinations of the copper-points:

Heycock and Neville,	1080.5
Stansfield.	1083
Holman.	1086
Holborn and Day.	1084.1

The value obtained by Holborn and Day is the only one determined directly in terms of the gas-thermometer.

Platinum.—(Fusion) 1780°. As the gas-thermometer has not been used above 1150° C., all higher fixed points must be reduced to the gas-scale by extrapolation. Although the uncertainty of this point is very considerable, perhaps over 25°, the determinations that have been made agree remarkably. Thus Violle, as well as Holborn and Wien, and Holborn again, all get 1780.

Iridium.—(Fusion) 2250°. Although it is questionable if temperatures of 2000° C. and over can be determined in terms of the gas-scale, it may, nevertheless, be found desirable to determine as exactly as may be one or more fixed temperatures in this range by other methods, as specific heat and the laws of radiation. Iridium and osmium seem to be suitable for this purpose. Hardly any limit of accuracy can as yet be placed upon such determinations. For iridium the following values have been found:

Violle.	1950° C.
Veder Weyde.	2200
Pietet.	2500
Nernst.	2200 to 2240
Rasch (computed).	2285

The recent development of furnaces suitable for use at these extreme temperatures will undoubtedly enable us to more sharply define this part of the scale.

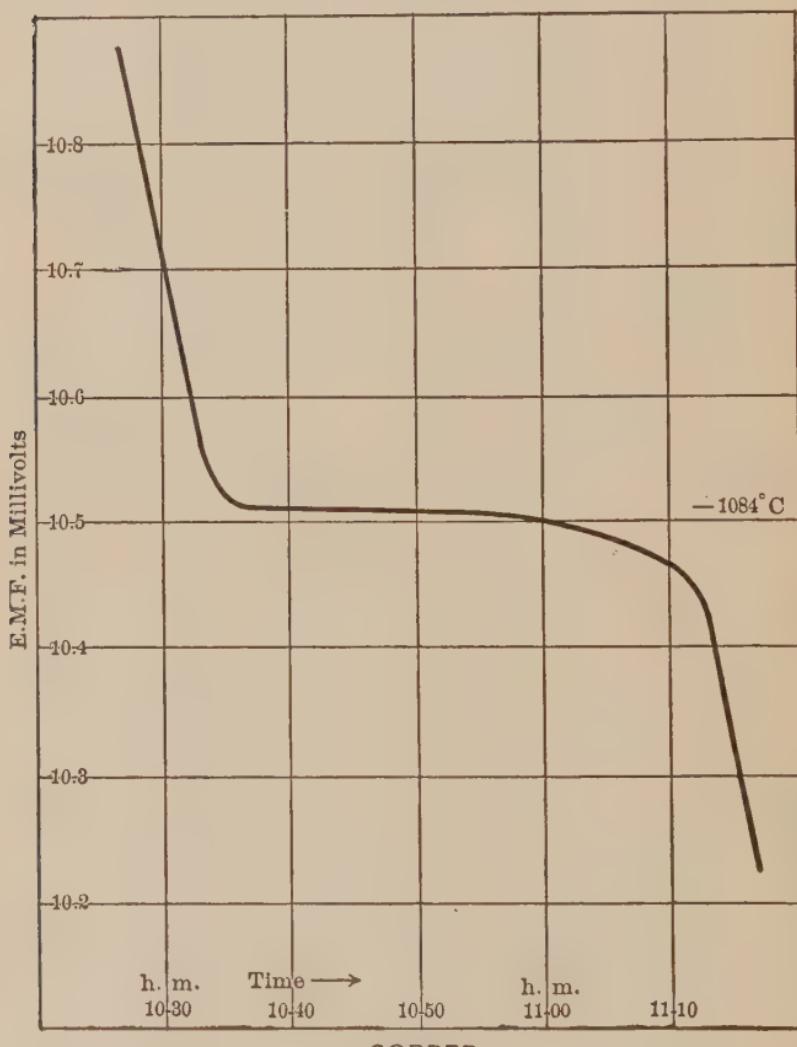
It is interesting to note that at the extreme temperature of the electric arc, 3600° C., the various radiation methods and the specific heat method give results agreeing to about 100° C.

Other metals have also been used in the attempt to determine fixed points and some of the results are given in the accompanying table:

TABLE OF FIXED POINTS.

Author.	Holman, etc. (corr. by G.K.B.)	D. Berthelot 1893-1901	Heycock & Neville Callendar 1895-99	Stansfield 1898	Holborn & Day 1900-1901
Instrument.	Thermocouple	Optical Interference	Electrical Resistance	Recording Thermocouple	Thermocouple and Nitrogen-ther.
Calibration data.	445°.0 1064	Expansion of air	0° 100° 444°.53	0° 100° 444°.53	Platinum-bulb Nitrogen-ther.
Sn.			231°.9	232°.1	
Bi.			269 .2	268 .4	
Cd.			320 .7		321°.7
[Pb].			327 .7		326 .9
Zn.			419 .0		419 .0
Sb.			629 .5		630 .6
[Cd].					
[Al].	654°.7	778°	645 .5	649 .2	657
[Zn].		918			
[Ag (in air)]. . .			955		955
Ag (pure)	962°.7 (1064)	962 1064	960 .7 1061 .7	961 .5 1062 .7	961 .5 1064 .0
Au.					
Cu (in air)					
Cu (pure)	1036			1080 .5	1083 .0
					1084 .1

The points which are uncertain or difficult of experimental determination are enclosed in brackets.



COPPER

FIG. 77.

The freezing-point curves of copper, antimony, and aluminium are shown in Fig. 77, where times in minutes

is plotted as abscissa and E.M.F. of a 90Pt-10Rh thermo-couple as ordinate. An inspection of the copper curve

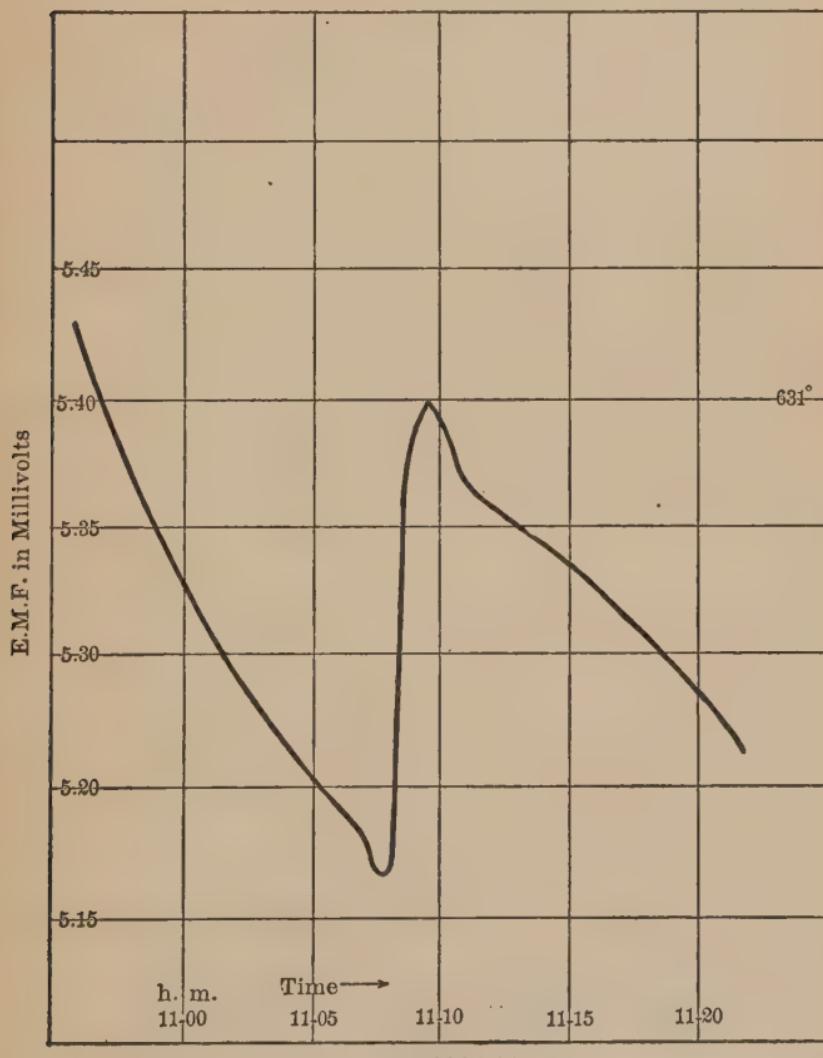


FIG. 78.

shows why this metal is desirable to use. With aluminum rapid cooling would be fatal to an exact determination,

and for this metal the melting curve is also given, showing the melting- and freezing-points to differ. Antimony under-

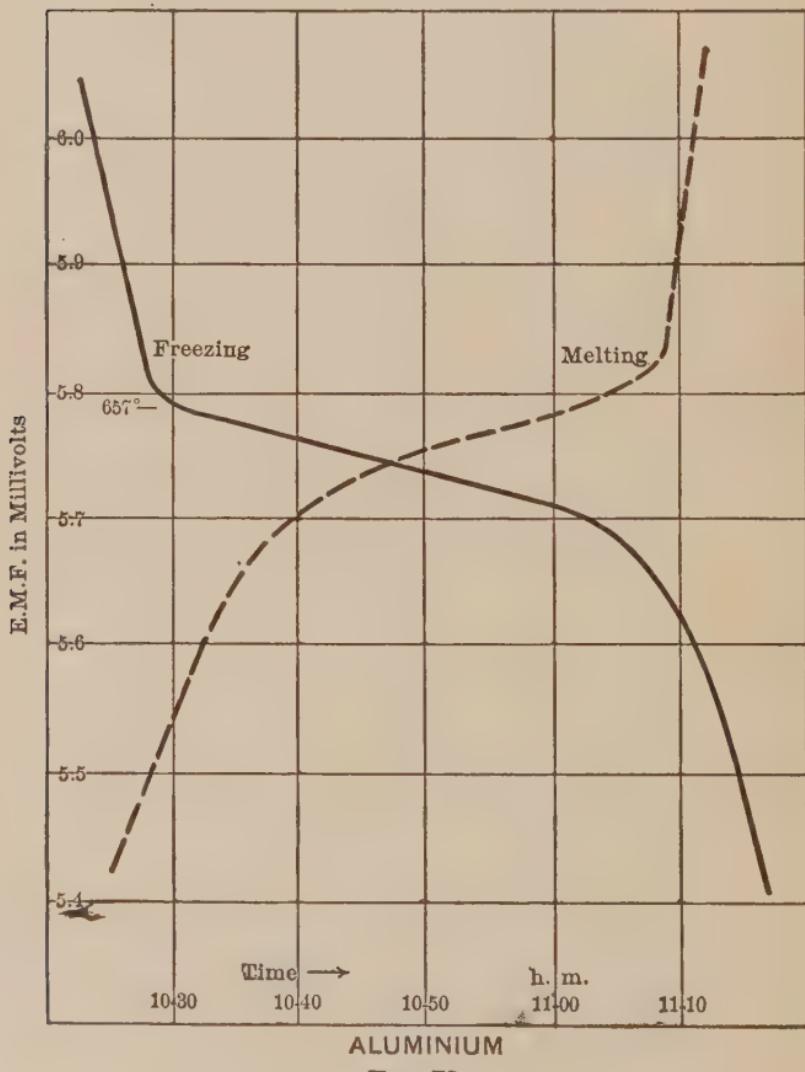


FIG. 79.

goes great undercooling, over 30° C., but the maximum is a very definite point.

Sometimes it is desired to calibrate a pyrometer down to room temperature, even if in this case the use of a mercury-thermometer is usually to be preferred. Use may be made of the boiling-points of water, aniline or naphthaline, and benzophenone, or of the tin freezing-point.

Water.—100° by definition, with a variation of 0°.04 for a change of 1 mm. in atmospheric pressure.

Aniline.—184°.1 with a change of 0°.05 per millimeter. This value is probably correct to 0.1 degree.

Naphthaline.—218°.0, with a change of 0°.06 per mm.

Benzophenone.—305°.9 with a change of 0°.075 per mm.

Metallic Salts.—The different fixed points that have been mentioned are not all of a very convenient use. It would be preferable to have in the place of the metals, metallic salts for the determination of the fixed points. These salts fortunately are for the most part without action on platinum, which is of great advantage for the standardization of thermocouples and resistance-thermometers. There are none, unfortunately, whose fusing-points have been determined up to the present time in a sufficiently precise manner.

Among the most interesting to study from this point of view, we may cite the following:

1 mol. NaCl + 1 mol. KCl.....	About	650°
NaCl.....	"	800
Na ₂ SO ₄	"	900
Pb ₂ O ₅ · 2Na ₂ O.....	"	1000
K ₂ SO ₄	"	1070
MgSO ₄	"	1150
SiO ₂ · CaO.....	"	1700

It is especially desirable to have a more satisfactory point than has as yet been obtained in the interval between the sulphur- and gold-points.

Table of Fixed Points.—In the actual state of our knowledge, the fixed points to which we should give preference are summarized in the table below:

	Boiling.	Freezing.
Water.....	100°.0	
Naphthaline.....	218 .0	
Sulphur.....	444 .6	
Tin	232°
Zinc.....	419
Silver.....	962
Gold.....	1065
Platinum.....	1780

Standardization of Pyrometers.—The above discussion has shown that we possess a number of fixed points which have been established with sufficient accuracy to use them in the standardization of pyrometers. For such standardization, two courses are open besides direct comparison with a gas-thermometer, a proceeding usually out of the question and furthermore rendered superfluous by the establishment of these fixed points. When its construction permits, a pyrometer may be calibrated by finding its indications at two or more of the fixed points, or may be compared with another which has been so calibrated. The latter method is the one used for ordinary purposes, as in the graduation of industrial instruments, but for pyrometers which are to be used as primary standards the former method should be used when possible.

We have discussed at some length, in their respective chapters, the methods of graduation for the various pyrometers and it is unnecessary to further dwell on this matter, except to say that it cannot be assumed that a

pyrometer once standardized is standardized for all time, especially if it has had hard usage.

Standardizing Laboratories.—Recognizing the importance of establishing, preserving, and disseminating a common and authoritative temperature scale and of providing means of having pyrometers and other instruments certified as to their accuracy, some of the governments have established laboratories, such as the Physikalische-Technische Reichsanstalt in Germany, the National Physical Laboratory in England, and the National Bureau of Standards * in the United States, whose

* The Bureau of Standards tests and gives certificates for any kind of pyrometer, and in this connection the following quotations, from Bureau Circular No. 7, on "Pyrometer Testing and Heat Measurements," may be of interest:

"When pyrometers are submitted for test, it is highly desirable that the request for test be accompanied by a statement giving as far as possible the conditions under which the pyrometer is used (*e.g.*, method of mounting pyrometer, depth of immersion, kind of bath or medium whose temperature is to be measured, how the pyrometer is protected, at what temperature it is used, and whether continuously exposed to these temperatures, etc.). A sketch showing method of use of instrument is often very useful. It is only when accompanied by such information that it is possible to realize approximately the same conditions in the test as in the actual use of the pyrometer and to make a statement as to the order of accuracy that may be attained. It also enables suggestions to be made as to desirable modifications in the use of the instrument that may lead to more satisfactory results. . . .

"It is desirable, when a thermocouple is submitted for test, that it be accompanied by the galvanometer with which it is used. The protecting sheaths should not be sent in.

"The complete test of a thermocouple consists in a thorough annealing at white heat, determination of the electromotive force of the couple at three or more known temperatures in terms of the standard scale of temperature of this Bureau, and the measurement of the resistance of the couple (when cold), with accompany-

functions are not only testing instruments but carrying on researches as well. The German institution, the oldest of these laboratories, has been one of the most potent factors in the development of excellency in German instruments, and has been of immense service to the industries as well as to the interests of science.

Electrically Heated Furnaces.—For the standardization of pyrometers as well as in many other high-temperature problems it is necessary to preserve a constant tempera-

ing tables of corresponding electromotive forces and temperatures, and when the pyrometer-galvanometer is submitted a table will be furnished giving temperatures directly in terms of the readings of the galvanometer joined to the couple. . . .

“The test [of radiation and optical pyrometers] consists in determining the readings of the instrument at three or more known temperatures in terms of the standard scale of this Bureau, together with a statement of directions and necessary precautions that should be observed in the use of the pyrometer. A table is also furnished giving temperatures in terms of readings of the instrument. . . .

“Testing of various kinds of calorimetric apparatus and thermal properties of fuels, oils, and other substances is undertaken by this Bureau. In cases of scientific or technical interest, special investigations in heat measurements and allied subjects will be carried out, such as the determination of coefficients of expansion at high temperature, specific heats, boiling-points, melting-points of metals, alloys, minerals, etc. . . .

“It is the desire of the Bureau to cooperate with manufacturers, scientists, and others in bringing about more satisfactory conditions relative to weights, measures, measuring instruments, and thermal constants, and to place at the disposal of those interested such information relative to these subjects as may be in its possession.

“It is also desired to aid in the solution of specific scientific problems arising in technical or scientific work, coming within the scope of the Bureau, and to this end correspondence is invited.

“Persons interested in pyrometric problems are welcome to visit the laboratories of the Bureau, where many of the leading types of pyrometers may be seen in operation.”

ture for a considerable time and to be able to reproduce a given temperature very exactly.

Electrically heated resistance-furnaces best serve these ends, and great improvements have been made in their construction in recent years.

Furnaces wound with nickel wire of 1 to 2 mm. diameter on porcelain have been used considerably, but they are slow in heating up and their upper limit is about 1200° C. if the furnace is to be used frequently, although for a single heating 1450° C. may be attained with care. Platinum wire has been used to attain higher temperatures, but the use of this material in wire form is very expensive for heating.

Heraeus has made electric heating to 1500° C. generally accessible by the substitution of platinum-foil for the wire, weighing about 1.5 grammes per square centimeter or having a thickness of about 0.007 mm. This reduces the cost of a platinum furnace very greatly, and has the further advantages of giving greater uniformity of heating and attaining safely higher temperatures than with wire-wound furnaces, and instead of taking an hour or more, five or ten minutes suffice to heat a foil furnace to 1400° C. Figs. 38 and 61 illustrate such furnaces. Above 1500° C. chemical action sets in between the platinum and material of the tubes tried thus far, so that although, as far as the platinum is concerned, 1700° C. could be maintained, yet the present upper limit for long periods of heating is 1500°.

For very high temperatures, up to 2100°, the iridium-tube furnaces of Heraeus may be used (p.169), as they have been with success by Nernst and others in the study of vapor pressures at these temperatures.

CHAPTER XIV.

CONCLUSION.

IN closing this account it will not be useless to call the attention of investigators to points whose study seems the most needed to aid the progress of our knowledge of high temperatures. We will mention first the precise determination of the fixed points serving for the graduation of pyrometers; there does not exist at the present time above the boiling-point of sulphur any temperature known certainly to 1° . For the ebullition of zinc, the fusing of silver and that of gold, which are at present the best known, the uncertainty may be 10° for the first, but is probably less than 5° for the fusing-points. It would be well also to try and find substances serving for fixed points that are more convenient to handle than the metals—salts, for example—which do not attack platinum either when they are melted or when they are vaporized; these substances should be found easily and economically in a state of purity; they should possess well-defined points of fusion and of ebullition, which is not always the case when the crystallized salt has several dimorphous varieties.

A second very important point for investigations of great precision would be the determination of the general form of the function which connects electrical resistance with temperature. One cannot hope to determine completely this function with the value of its parameters, because there are not two samples of platinum having

exactly the same resistance; it is necessary in each case to make the calibration by means of fixed fusing- or boiling-points. The work of Heycock and Neville is a long step towards the accomplishment of this end. The number of such points to compare depends on the number of parameters contained in the formula. By his researches in this matter, Prof. Silas Holman greatly facilitated the use of thermoelectric couples by showing that it is sufficient between 0° and 1800° to use a logarithmic formula containing only two parameters.

For the measurement of exceedingly high temperatures, which can be effected only by methods employing radiation and depending upon extrapolations often considerable, it would be very useful to determine, with greater precision than has been done as yet, the law of the radiation from a rigorously black body (enclosed space), either for a monochromatic radiation, as radiation transmitted by the red glasses, or for the totality of heat radiations. But such a study can be of value only on the condition of possessing a very great precision, difficult to attain actually on account of the uncertainty which still exists as to the temperatures directly measurable. Great advances have been made in this field of pyrometry in recent years by Paschen, Lummer and his associates at the Reichsanstalt on the experimental side, and by Wien, Boltzmann and Planck on the theoretical side.

The Stefan-Boltzmann law has been shown to apply from -200° C. up to 1600° C., with an accuracy of better than one per cent for total radiation. Wien's spectral energy law and his displacement law for monochromatic radiation are in exact agreement with the preceding certainly up to 2000° C., and probably at the temperature of the arc, 3600° C., and no certain discordance has been found in the results using these various methods in the

estimation of the effective temperature of the sun, about 6000° C. Le Chatelier's formula for monochromatic light seems also to be in agreement with the others. The experimental comparison and verification of these formulae have been greatly facilitated by the development of electric-resistance furnaces, and a convenient form of experimental black body.

The establishment of a satisfactory temperature scale to 2000° C. and beyond is perhaps the most pressing problem in pyrometry to-day, as witness the temperatures realized in the Moissan furnace, the thermite process, and many pyrochemical and metallurgical operations. The laws of radiation, we have seen, will serve as a tentative scale, which is, however, without significance as an extension of the gas-scale proper, as the degrees of temperature measured optically in this high range may or may not have any relation to those given by a gas-thermometer. It may be possible, however, to intercompare other methods with the radiation. Thus Berthelot's system of gas-thermometry can undoubtedly be carried higher successfully. Again, purely thermodynamic and also chemical methods of measuring extreme temperatures have been suggested, among others by Nernst, who would make use of the expression involving the dissociation of a gas as follows:

$$Q = RT^2 \frac{d \log K}{dT},$$

where Q is the heat of formation of carbonic acid at the temperature T , R the gas constant, and K the coefficient of mass action, which is dependent upon the pressure and degree of dissociation of the gas mixture.

Finally, if the intensity of radiation per unit area could be exactly determined in C.G.S. units, as was tried by

Lummer and Kurlbaum, still another absolute scale would be had. At very high temperatures, this method is more promising than at lower, because the light-intensity increases relatively less rapidly.

At the Paris congress of 1900, Barus thus summarized recent progress: The actual state of pyrometry is most encouraging. It is clear that in a few years from now pyrometry will be in possession of a series of constants as exact as those of the best-developed branches of physics. In Germany, a gas-thermometer impermeable to the thermometric gas and rigid up to white heat has been found, thanks to the efforts of Holborn, Wien, and Day, at the Reichsanstalt. In England, the efforts of Callendar, Griffiths, and others to construct an instrument of remarkable sensibility from the absolute zero to 1000° C. have been crowned with merited success.

In France, the best practical pyrometer has been found by Le Chatelier, and D. Berthelot has devised an optical method for the measurement of temperatures in absolute value, independent of the form and size of the thermometric envelopes, and whose upper limit is indefinite; for since we have learned, thanks to the great discovery of Nernst, that the refractory earths become conductors at high temperatures, it has become possible to heat electrically the most infusible substances up to the highest degrees on the scale.

With a thermostat of this kind, Berthelot's pyrometric method in absolute value marches side by side with the most advanced practical progress realized by Moissan; in other terms, pyrometry in absolute value is only limited to-day by the difficulty of the manufacture of apparatus in refractory materials.

In closing we beg to call attention to a fact of some importance. The measurement of high temperatures

possesses certainly great interest from the point of view of the progress of pure science; but it is to be noted that industrial needs have stimulated the partial solution of this problem: Wedgwood, the china manufacturer, seeking to better his processes; similarly, Seger, at the Berlin works, occupied himself exclusively with ceramic products; Siemens sought to regulate the making of steel; the engineers of the Paris Gas Company wanted a means of control over the distillation of oil; Le Chatelier studied the thermoelectric pyrometer in the course of investigations on the baking of clay and on the manufacture of cements; he studied the optical pyrometer at the request of a Sheffield steel manufacturer, Hadfield, who desired for his works a pyrometer uniting accuracy with simplicity of use. Roberts-Austen, director of the mint at London, devoted all his efforts for many years to the study of industrial alloys, obtaining results of great value, largely due to the utility of the recording-pyrometer.

This incentive of practical needs on the progress of science is not surprising. The savants who founded chemistry recognized no distinction between pure and applied science. Lavoisier, Chevreul, Gay-Lussac, Dumas, Thénaud, H. Sainte-Claire-Deville went indifferently into the laboratory or the works. It is the present trend of our teaching methods that has opened a breach increasing in size every day between theory and practice.

In the scientific laboratories all efforts follow in well-beaten paths. There one is free to choose his subjects of study according to his caprices; one may be easily guided by artificial preoccupations, concerning themselves but very indirectly with a study of nature. Finally, one may have confidence for a long time in erroneous results without having any inkling of the error committed. In industrial works it is quite otherwise: one cannot remain

stationary upon problems already solved; in spite of one's self one must march ahead. Subjects of study obtrude and must necessarily be taken up in the order of their real importance. Wrong conclusions are made evident by their contradictions at each instant with facts that one cannot refuse to see. These conditions explain how laboratories attached to industrial works, with their insufficient personnel absorbed largely in other matters, with their rudimentary material, come nevertheless to contribute largely to the process of pure science. All the progress so important in the chemistry of iron is made to-day in industrial works and in the laboratories attached to them.

It is not in chemistry alone that practical needs have manifested this creative power. It was in studying the boring of cannon that Rumford met the notion of the conservation of energy; it was in reflecting upon the steam-engine that Sadi-Carnot established the basis of thermodynamics; it was in seeking to perfect light-house lenses that led Fresnel to his investigations on the theory of light.

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